October, 1934

RUBBER CHEMISTRY AND TECHNOLOGY

Published under the Auspices of the
RUBBER DIVISION *of the* AMERICAN CHEMICAL SOCIETY

VOLUME VII NUMBER 4

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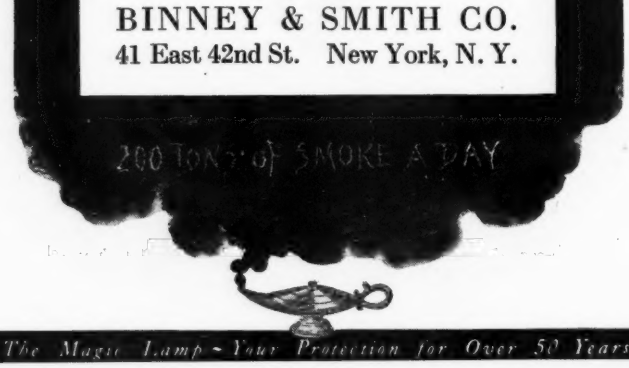

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RUBBER CHEMISTRY AND TECHNOLOGY

Published quarterly under the Auspices of the Rubber Division
of the American Chemical Society,
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Vol. VII October, 1934 No. 4

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RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the editor representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

Rubber Chemistry and Technology may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Rubber Division upon payment of the dues ($2.00) to the Division and thus receive Rubber Chemistry and Technology.

(2) Any one who is not a member of the American Chemical Society may become an Associate Member of the Rubber Division (and also a member of his local group if desired) upon payment of $4.00 per year to the Treasurer of the Rubber Division, and thus receive Rubber Chemistry and Technology.

(3) Companies and Libraries may subscribe to Rubber Chemistry and Technology at a subscription price of $6.00 per year.

All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers, and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, C. W. Christensen, Easton, Pennsylvania, or Rubber Service Laboratories, Inc., Akron, Ohio.

Articles, including translations and their illustrations, may be reprinted if due credit is given Rubber Chemistry and Technology.

Rubber Division Activities

The Rubber Division of the American Chemical Society

Officers

Chairman.....SIDNEY M. CADWELL, United States Tire Co., Detroit, Mich.
Vice-Chairman.....H. E. SIMMONS, Akron University, Akron, Ohio
Secretary-Treasurer.....C. W. CHRISTENSEN, Rubber Service Laboratories, Akron, Ohio
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Sergeant-at-Arms.....L. W. BROCK

The Meeting of the Rubber Division in Cleveland, September 12 and 13, 1934

The Rubber Division met in the Higbee Auditorium, Cleveland, Ohio, on September 12 and 13, with three hundred in attendance.

Presentation of Papers

1. Norman Bekkedahl. Forms of Rubber as Indicated by Temperature-Volume Relationship.
2. R. S. Jessup and A. D. Cummings. Heats of Combustion of Rubber and of Rubber-Sulfur Compounds.
3. J. T. Blake. Studies in the Vulcanization of Rubber. VI. Thermochemistry.
4. C. E. Barnett and W. C. Mathews. Thermal Properties of Rubber Compounds. II. The Effect of Pigmentation of the Heat Generation of Rubber Compounds.
5. R. S. Havenhill and W. B. MacBride. A New Laboratory Machine for Evaluating Breakdown Characteristics of Rubber Compounds.
6. Harlan A. Depew and M. K. Easley. The Surface Energy Relations between Pigment Materials and Rubber.
7. C. R. Park and V. N. Morris. Dispersion of Channel Gas Black in Rubber. Effect of Stearic Acid and Other So-called Dispersion Agents.
8. Thomas Midgley, Jr., A. L. Henne, A. F. Shepard, and Mary W. Renoll. Natural and Synthetic Rubber. XV. Oxygen in Rubber.
9. W. F. Busse. Some Relations between the Tear Resistance and the Structure of Rubber.
10. J. H. Dillon and P. M. Torrance. A Method for Measuring the Pressure in a Rubber Extruding Machine.
11. George A. Sackett. The Effect of Manganese Salts on Vulcanized Rubber.
12. C. S. Powell and J. N. Street. Value of Antioxidants in Counteracting the Detrimental Effects of Copper-Contaminated Rubber.

13. Ira Williams. Colloidal Changes during Vulcanization of Rubber.
14. W. B. Wiegand. Higher Alcohols in Rubber Compounding. II. Glycerol.

Business Meeting and Election of Officers.

On the evening of September 12, the Division enjoyed a dinner and entertainment in the Rainbow Room of the Carter Hotel, with 396 in attendance. The Dinner Committee consisted of V. L. Smithers, *Chairman*, Enos Baker, J. N. Street, H. B. Protheroe, Bert Taylor, and C. A. Carlton, and they are to be congratulated for providing a fine dinner and entertainment. The following companies are to be thanked on behalf of the Division for their contribution of fine souvenirs:

Akron Chemical Company	E. I. duPont de Nemours Co.	New Jersey Zinc Co.
Anaconda Zinc Oxide Co.	Farrell-Birmingham Co.	Rubber Service Laboratories Co.
American Zinc Oxide Co.	General Atlas Carbon Co.	
Binney & Smith	C. P. Hall Co.	Stauffer Chemical Co.
Godfrey L. Cabot Co.	J. M. Huber Co.	Superior Zinc Co.
Columbia Chemical Co.	Imperial Color Co.	United Carbon Co.
Dow Chemical Co.	Naugatuck Chemical Co.	R. T. Vanderbilt Co.
Wishnick-Tumpeer, Inc.	Xylos Rubber Co.	C. K. Williams Co.

At the close of the papers, a general business session of the Division was held, at which time the Secretary made the following report:

Secretary's Report

Total membership, Sept. 8, 1934		452
Members paid for 1934	357	
Associate members for 1934	95	
New members and associate members for 1934 (included in above figure)	48	
Total membership not paid for 1934		32
Members unpaid for 1934	24	
Associate members unpaid for 1934	8	
New members for 1933 who did not renew for 1934	4	
Subscriptions paid for 1934		104
Subscriptions not renewed for 1934		9
Honorary members and exchanges		32

H. E. Simmons, *Secretary*

Treasurer's Report

In bank at St. Petersburg meeting	$3020.64	
Received from dues and subscriptions	368.80	
Received from advertising	1265.30	
Received from Rubber Manufacturers' Assn.	1500.00	
Received from surplus at St. Petersburg banquet	44.04	
		$6198.78

Expenses		
Mack Printing Company	$3772.69 (January, April, July)	
Translations	385.83	
Expenses of Secy.-Treasurer to St. Petersburg meeting	138.00	
Postage, telegrams, telephone calls, office supplies	16.96	
Secretarial Services (6 months)	60.00	
Circular letter regarding Cleveland meeting	9.75	
Foreign check to be deducted	4.00	
Tax on checks written (15 at 2¢)	0.30	
Tax on English check	0.75	4388.28
Money in the bank, Sept. 8, 1934		$1810.50
Money in liquidation bank	$2436.05	
Money for advertising in the July issue of RUBBER CHEMISTRY AND TECHNOLOGY not received	198.55	2634.60
Total		$4445.10

H. E. SIMMONS, *Treasurer*

New Officers

A Nominating Committee, appointed by the Chairman, and consisting of Stanley Krall, W. W. Vogt, and H. A. Winkelmann, made its report, following which a ballot showed the election of the following officers to serve the Division for the coming year: S. M. Cadwell, *Chairman*, H. E. Simmons, *Vice-Chairman*, C. W. Christensen, *Secretary-Treasurer*, L. W. Brock, *Sergeant-at-Arms; Executive Committee:* Ira Williams, A. A. Somerville, H. C. Conroy, J. N. Street, G. K. Hinshaw.

H. E. SIMMONS, *Secretary-Treasurer*

Minutes of the Newly Elected Executive Committee, September 13, 1934

W. B. Wiegand appeared before the Executive Committee and discussed the possibility of inviting representatives from the Rubber Research Institute of Malaya to meet with the Rubber Division at one of its Annual Meetings each year. Mr. Wiegand was instructed to correspond with Hon. Dr. H. A. Tempany, Director of Agriculture, Singapore, Malaya, expressing the willingness and pleasure of the rubber chemists of America to join with the British in such a meeting. It was voted that details for such a meeting would be worked out between the proper officials in the Far East and the Chairman of the Rubber Division.

The question whether or not the Rubber Division would meet with the Society in the Fall of 1935 came up for general discussion. It was decided that final decision with reference to this matter would be left until the spring meeting in New York.

C. C. Davis, Editor of RUBBER CHEMISTRY AND TECHNOLOGY, discussed with the Executive Committee the earlier proposal to publish a book on rubber, in the form of an A. C. S. Monograph. The Executive Committee unanimously voted

the following resolutions: that C. C. Davis be appointed Editor-in-Chief of this A. C. S. Monograph on Rubber; that he is to have full authority to create his own editorial staff and further authority to select the authors, and that the Rubber Division will underwrite the expenses which will be incurred in publishing the Monograph, in an amount not to exceed $100.00 up to the time of the New York meeting, subject to the approval of the Treasurer.

The Executive Committee instructed the Chairman to interview C. L. Parsons, Secretary of the American Chemical Society, relative to the Division holding its autumn meeting in 1935 at some time and place other than those of the regular Society.

The Chairman appointed A. A. Somerville as Chairman of the Entertainment Committee for the New York Meeting.

The Executive Committee voted to hold the Rubber Division meeting in New York on Monday and Tuesday, with the Rubber Division dinner on Monday night, of the week of the general meeting.

C. W. CHRISTENSEN, *Secretary-Treasurer*

New Books and Other Publications

Eighteenth Report on Native Rubber Cultivation. Prepared by the Bureau of Agricultural Economics, Department of Economic Affairs, Batavia, Java. 1934, 10 pp.

Covering the first quarter of 1934, this report points out the causes behind the rise in standard sheets from 13.8 guilder cents per $^1/_2$ kilogram in December, 1933, to 16.3 guilder cents per $^1/_2$ kilogram in March, 1934. Local reports from various sections of the Dutch East Indies colonies are included. [From *The Rubber Age* of New York.]

Eleventh Annual Report. The Technical Department of the International Association for Rubber and Other Cultivations in the Netherlands Indies. Published by the Association. 12 pp. 1933. For free distribution.

Experiments conducted by technologists of the International Association during 1933 dwelt particularly with mixtures of rubber and asphalt. Generally these two liquids can be mixed together in any proportion with the exception of certain emulsions where a homogeneous mixing can only be obtained after the addition of protective colloids or stabilizers. Investigations relating to asphalt-rubber mixtures, obtained after evaporation of the mixture of liquids, showed that the properties of the original asphalt improved in the rise of melting point, diminished tendency to flow, increased resistance against pressure, increased resiliency and increased adhesive power to gravel. A rubber powder prepared with dextrin proved to absorb moisture easily from the atmosphere. Tests were conducted in connection with chlorinated rubber. Another series of tests was conducted with building boards of latex and fibrous materials and data collected as regards machinery with which these products can be made. Brief mention is made in the report of these and other experiments made during 1933. [From *The Rubber Age* of New York.]

Rubber: A Statistical Appraisal. Published by F. R. Henderson, 25 South William Street, New York City. 7 pp. 1934. For free distribution.

Replete with maps, charts, and diagrams, Mr. Henderson's latest survey of the rubber industry attempts to dispel the doubts and fears which still persist in the minds of some connected with the industry. This appraisal analyzes several important factors that bear a relationship to prevailing conditions since the enactment of the new restriction scheme. Detailed figures on world consumption and absorption of rubber occupy the major portion of the appraisal. [From *The Rubber Age* of New York.]

Rubber. Published as a special section of the July 16 issue of *The Financial News*, 20 Bishopsgate, London, E.C. 2, England. 32 pp. 1934.

Each year *The Financial News* publishes this special section devoted to rubber and rubber products. The current edition carries a number of interesting articles including "The Rise of the Rubber Industry," by H. Eric Miller; "Rubber Regulation," J. G. Hay; "Research and the Plantation Industry," Sir Herbert Wright; "Latex—Its Nature and Method of Extraction," G. E. Coombs; and additional timely articles written by internationally known rubber authorities. [From *The Rubber Age* of New York.]

The Situation in Crude Rubber. Munds, Winslow & Potter, 40 Wall St., New York, N. Y.

In this 4-page bulletin the crude rubber condition is reviewed as to production and consumption under restriction. visible rubber stocks, the price ob-

jective of producers, and its results on the market. [From the *India Rubber World.*]

Rubber—Aspects of the Future Outlook. Distributed by Bankers Economic Service, 91 Wall Street, New York City. 1934.

Another discussion on the probable effects of the restriction scheme. The author, J. Luck, uses charts and graphs to show recent trends in production and consumption of rubber throughout the world, and predicts a successful conclusion for the restriction plan. Chart comparison is made in this report between the former Stevenson Restriction Scheme, and the current position of rubber. [From *The Rubber Age* of New York.]

Kautschuklacke und Kautschukkitte. By Otto Merz. Published by Union Deutsche Verlagsgesellschaft, Zweigniederlassung, Berlin, Germany. Cloth, 170 pages; 6¼ by 9¼ inches. 40 tables, 14 illustrations.

In collecting data on rubber varnishes and cements, Otto Merz has performed a service for which the rubber industry owes him a hearty vote of thanks. He presents his material in 20 concise chapters treating source and harvesting of rubber, gutta-percha, and balata; Thermoprene; chlorinated rubber; solvents; rubber emulsions; accelerators; different types of rubber varnishes; latex paints; varnishes from thermoprene and chlorinated rubber; varnishes without rubber for rubber goods; rubber cement; varnishes and cements from resins of rubber, balata, and gutta-percha, etc. A number of formulas are given, also numerous references to articles and patents.

The indices of authors, subjects, and patents, the good paper, clear print, and neat, strong binding all help to make the little volume a worth-while addition to the rubber library. If one criticism is permitted, it must be that the data referring to latex could have been more ample. [From the *India Rubber World.*]

1934 Year Book & Code Guide. The National Association of Waste Material Dealers, Inc. Published by the Association, Times Building, New York City. 286 pp. 1934. $2.00.

Carries all the approved classifications covering the waste material trade, a special wood pulp section, all trade customs of the waste material trade, special code sections and the personnel of many code authorities. Standards of scrap rubber specifications and packing of the Rubber Reclaimers Association, Inc., are contained in the volume, in addition to the Code of Fair Competition for the reclaimed rubber manufacturing industry. The book accomplishes its purpose as a guide to waste material dealers and allied industries. [From *The Rubber Age* of New York.]

Onward from the Beginning. An historical sketch of the Royle tubing machine. By Vernon Royle, president of John Royle & Sons, Inc., Straight and Essex Sts., Paterson, N. J. Paper, 103 pages; 6 by 9 inches. Illustrated.

The author introduces his account of the origin and development of the Royle tubing machine line, with some very interesting personal recollections of incidents relating to the reception of the early machines and the secrecy with which their performance was surrounded by the rubber manufacturers who used them.

The developments recorded in the text and photographic reproductions cover a half-century of progress in the design and construction of tubing machines and appliances for dealing with rubber, celluloid, etc., by the extrusion process. The latter half of the book deals with tubing heads and fixtures, insulating heads and fixtures, strainer heads, cylinders, stock screws, driving gears, thrust

bearings, motor drives, take-off mechanisms, lubrication, celluloid, plastics, and welding wire coating.

The book is a summary of accomplishment in well-designed tools that mean much to the rubber industry. [From the *India Rubber World.*]

Chemical Guide Book. Published by Chemical Markets, Inc., 25 Spruce Street, New York City. 695 pp. 1934. $2.00.

The Tenth Edition of this chemical guide is divided into four sections and includes a catalog of leading chemical firms; a buying guide and directory of chemical and allied products arranged alphabetically with names and addresses of sources of supply; a geographical directory of the chemical and allied industries; and a chemical statistics section showing high and low prices for the years 1932 and 1933 on more than 1500 heavy and fine chemicals, intermediates, and allied products. A detailed list of trade associations in the chemical and allied industries is also included in the concluding pages of the guide book. [From *The Rubber Age* of New York.]

[Translated for Rubber Chemistry and Technology from the Atti della Reale Accademia Nazionale dei Lincei, 6th Series (Rendiconti, Classe di Scienze fisiche, matemiche e naturali), Vol. 19, No. 4, pages 206–211, February 18, 1934.]

The Structure of Gutta-Percha Based on Studies with Electron Rays

G. Bruni and G. Natta

INSTITUTE OF GENERAL CHEMISTRY OF THE ROYAL POLYTECHNIC AT MILAN, ITALY

Among the natural organic compounds with high molecular weights which have been the object of roentgenographic investigations with a view to determining their intimate constitution, rubber and other hydrocarbons of similar constitution such as gutta-percha and balata have been extensively studied in recent years.

The results obtained with these substances by x-ray methods have however not been so complete and reliable as in the case of other products with high molecular weights, such as cellulose, found in nature in ramie and in certain vegetable fibers in forms which are particularly well oriented, which is of enormous advantage in structural investigations.

Nevertheless, the roentgenographic results on rubber are of the greatest interest because from them it is possible to show that the molecules of rubber are oriented when the rubber is stretched or frozen, so that it can be proved that under these special conditions it has a sort of crystalline structure which is characterized by definite identity periods. The determination of the identity period in the direction of the fibers, which is 8.1 A. U., is particularly reliable.

According to Mark and Susich[1] the periods of identity for the two other directions should be 12.3 and 8.3, respectively, and the structure should be rhombic.

Unlike rubber, gutta-percha and balata should be crystalline even at ordinary temperature, and in the unstretched condition[2,3] and according to Hauser[4] should have the same structures, and give identical roentgenographs.

Susich and Hopff[5] moreover observed that gutta-percha is transformed at 40° (the pure hydrocarbon at 60°) into a modification which in the unstretched state is amorphous and becomes crystalline when stretched, giving photographs which denote a fibrous structure.

The stable modification at ordinary temperature is called α-gutta-percha, that stable at elevated temperatures is β-gutta-percha. The latter form in the stretched condition shows an identity period in the direction of the fibers of 4.73 (or 9.46) A. U., whereas the other has a period of 4.96 A. U.

Stillwell[6] and Clark[7] studied numerous samples of balata from different sources and, contrary to Hauser, found differences in the photographs of the two products, which they explain by assuming that gutta-percha is a mixture of the crystalline balata hydrocarbon and of another crystalline component.

In spite of numerous roentgenographic investigations, the results obtained up to now are limited (1) to a more or less uncertain estimate of the identity period in the direction of the fibers and (2) to proving that gutta-percha and balata have a structure different from that of rubber. The physical properties of gutta-percha and of rubber, and the fact that in both compounds the molecules of the hydrocarbons present are made up of groups of isoprene radicals, have led Staudinger[8] to assume that the difference in constitution in the two hydrocarbons may be due solely to the *cis*-configuration of one and to the *trans*-configuration of the other.

Mark ascribes the *trans*-configuration to gutta-percha, because it is less easily fusible.

With the aim of completing the limited knowledge of the structure of gutta-percha we have in the present work studied this substance by a method based on the interferences of high velocity electron rays. This method has the advantage over x-ray methods of still furnishing photographs with clear lines when the crystals of the substance examined are so small that they give with x-rays only very cloudy bands, whose maxima are not clearly determined. Other advantages are the rapidity of the exposure and the fact that the radiations are monochromatic, which are particularly useful with structures which are complex or which deteriorate easily, *e. g.*, gutta-percha, because of its tendency to oxidize.

The apparatus used in the investigations with electron rays was that of Seemann,

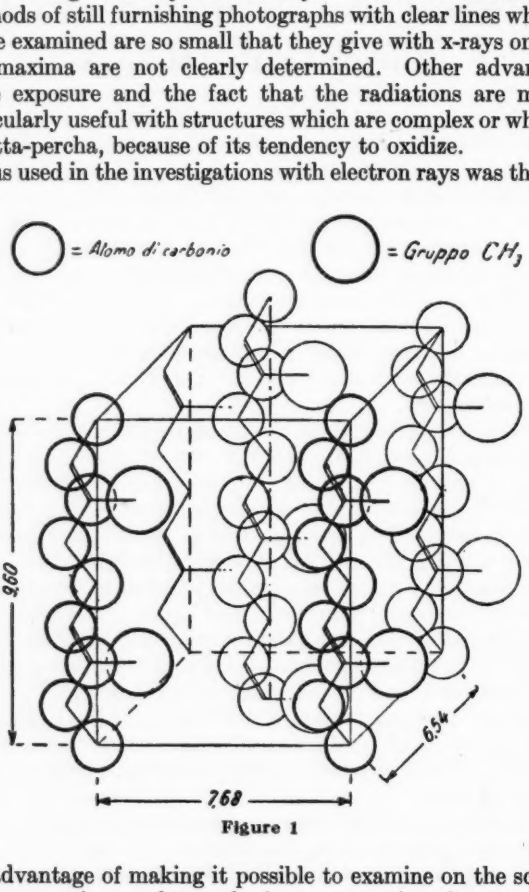


Figure 1

which has the advantage of making it possible to examine on the screen the interferences of the preparations and to make four consecutive photographs of different preparations, the apparatus being under high vacuum all the time.

If several drops of a very dilute solution of gutta-percha in benzene are allowed to fall on a large surface of water, there are obtained after evaporation of the benzene thin films of gutta-percha 0.5×10^{-5} to 3×10^{-5} cm. thick. Such films of gutta-percha generally tend to break or to wrinkle if they are removed from the surface of the water. It is possible however by means of thin copper plates (0.1 mm.), which are pierced with holes of 1 to 1.5 mm. and which are immersed in the water under the films, to lift out small portions of such films, some of which are of a thickness that renders them suitable for an examination by transparency by high-speed electron rays.

It is known that for the examination by transparency with electrons of sufficiently high velocity (λ = 0.04 to 0.05 A. U.), the samples ought to have a thickness

around 10^{-5} cm. so as not to be wholly opaque to the incident rays, and samples of metals must be at times only 10^{-6} to 10^{-7} cm.

In this experiment, the Seemann apparatus was provided with a device which made it possible to carry out all the operations under a high vacuum, to rotate the apparatus on both a horizontal and a vertical axis and to move it vertically during the experiment.

Such a device was found to be extremely advantageous in the examination of gutta-percha, since it was observed during the examination that the lines of interference of gutta-percha, visible on the fluorescent screen, enlarge and then disappear completely after a few seconds or after a few fractions of a second of illumination with the electron rays.

This phenomenon, the first observed with electron rays up to now, is particularly surprising in the rapidity with which it may be verified. It was proved that the action of electron rays transforms crystalline gutta-percha rapidly into the amorphous form. The transformation is irreversible, because when the electron rays are interrupted for about ten minutes the film does not become crystalline again, but is completely amorphous when it is again examined at the same point.

This transformation may be compared with that observed by Hopff and Susich (*loc. cit.*) of α-gutta-percha into β-gutta-percha when the former is heated above 40° C. It is probable that the transformation observed with electron rays does not depend upon a photochemical action of the electron rays or upon a mechanical action, but rather upon a secondary thermal effect by the heating which accompanies the absorption of the unreflected electron rays. Because of the high vacuum in the apparatus during the experiment with electron rays, because of the thinness of the samples and because of their low conductivity, it is possible that the temperature of the film of gutta-percha is able to rise rapidly in the illuminated portion to above 40° C., the transformation point of α-gutta-percha, which is crystalline even when it is not stretched, into that of β-gutta-percha, which is amorphous in the unstretched state.

In spite of this rapid disaggregation of the crystalline lattice by the action of electron rays, it was possible to obtain some very fine photographs of α-gutta-percha by always keeping the film in movement during the experiment, in such a way that the rays illuminated different parts of the film in succession and at every point for a shorter time than that necessary to cause perceptible transformation of α-gutta into β-gutta-percha.

The photographs contained about a dozen lines. Three photographs, taken with different samples, gave exactly the same lines of the same intensity and in the same position. The times of exposure, maintaining the film in motion in the plane normal to that of the incident electron rays, were from two to four seconds. The voltage (72 kw.) corresponds to a wave length of 0.044 A. U., which was determined exactly by means of photographs of sodium chloride.

This table gives the results of the calculation of one of the best photographs obtained. It is evident that the first three lines are very strong, whereas the others are all much weaker. On the supposition that these three lines correspond to the first reflections of like order of normal lattice planes for the three fundamental identity periods, it is also possible to arrange easily, for indices which are even and correspond to small values, all the other lines in the photograph. The fact that besides the lines (002), (020), (200) fixed arbitrarily by us, there are also present lines (022), (202), (220) with similar intensities, and lines (222), (040), (400), (040) and (024), in other words almost all those which correspond to the smallest even indices, the fact that the lattice constants calculated for all the reflections agree, and that there is no line present which it was not possible to

TABLE I

PHOTOGRAPHS BY ELECTRON RAYS OF α-GUTTA-PERCHA

λ = 0.044 A. U. Distance of the sample from the plate = 422 mm.

Diameter of the Interference Rings	Intensity	tan θ	d Experimental	h k l	d Theoretical per a = 6.53
7.7	ff	9.12	4.82	0 0 2	4.81
9.6	ff	11.38	3.86	1 0 2 0 2 0	3.86 3.84
11.3	f	13.39	3.28	2 0 0	3.27
12.6	d	14.93	2.95	0 2 2	2.99
13.8	dd	16.35	2.69	2 0 2	2.70
15.0	ddd	17.77	2.48	2 2 0	2.48
15.3	ddd	18.13	2.42	0 0 4	2.40
16.3	ddd	19.79	2.22	2 2 2	2.21
18.2	ddd	21.56	2.04	0 2 4	2.03
19.6	d	23.22	1.90	0 4 0	1.92
22.7	dd	26.90	1.64	4 0 0	1.63
30.0	d	35.55	1.24	4 4 0	1.24

arrange, make the supposition highly probable. Our hypothesis is confirmed by a calculation of the volume of the elementary cell, by the number of the isoprene radicals contained in this volume, and by the calculated value of the density.

The fundamental identity periods result:

$$a = 6.53$$
$$b = 7.68$$
$$c = 9.60$$

The axial ratios corresponding to a rhombic or a pseudo-rhombic structure are then:

$$a:b:c = 1:1.176:1.47$$

The resulting volume of the elementary cell is 481×10^{-24} cc. On the assumption that the cell contains 4 isoprene groups, the resulting density is 0.94. This is in perfect accord with the most recent experimental data. As a matter of fact Dean[9] found for balata and for gutta-percha at 24° C. densities ranging from a minimum of 0.943 to a maximum of 0.954.

The identity period of 9.60 A. U. along the *c* axis agrees with that calculated by Meyer and Mark[10] from the works of Hauser and Susich, which corresponds to the length of a chain composed of two isoprene radicals in *trans*-configuration.

On the supposition that the distance between two atoms of carbon united by a simple bond is equal to 1.55 A. U. and that the angle between the valences is 109° 30′, and on the further supposition that the distance between the nuclei of the two atoms of carbon united by a double bond is equal to 1.20 A. U. and that the angle between the direction of the double bond and that of the adjacent simple bond is 120°, then the length of an isoprene chain in *trans*-configuration is 3 (1.55 *sin* 54° 45′) + 1.20 *sin* 60° = 4.83 A. U., which agrees with the experimental value of 4.80 A. U.

Although all the indices are divisible by two, in other words though the experimental values point to a cell having bases one-half of those indicated, the cell must nevertheless be assumed to have a double base, because otherwise it would not contain a whole number of isoprene groups.

The absence of reflections with odd indices makes very probable a centrated structure.

In view of the nature of the long chain molecules, a fibrous centrated structure

is probable, *i. e.*, a structure of such a character that its projection on a plane normal to the axis of the fibers (the *c* axis in the present case) is centrated.

The accompanying figure represents diagrammatically a type of structure which is in accord with the experimental results and with the considerations above. A confirmation of such a structure is not possible because of the intensity of the interferences, since the photographs show a too limited number of reflections.

The experimental results can also be in accordance with an identity period *c* of 4.80 A. U. which is one-half the value previously assumed. In this case the other two identity periods would remain unaltered, and the cell with a volume one-half of that previously assumed would then contain two isoprene groups. In such a case the third index would be one-half as great, which results in an odd number, while the first indices correspond only to even numbers. This is still in accord with the hypothesis of a fibrous structure.

References

[1] Mark and Susich, *Kolloid Z.*, **40**, 11 (1928); Meyer and Mark, *Der Aufbau der Hochpolymeren Organischen Naturstoffe*, Leipzig, **1930**.

[2] Clark, *Ind. Eng. Chem.*, **18**, 1131 (1926).

[3] Ott, *Naturwissenschaften*, **14**, 320 (1926).

[4] Hauser, *Kautschuk*, **3**, 228 (1927); Hauser and Rosbaud, *Ibid.*, **3**, 17 (1927).

[5] Hopff and Susich, *Kautschuk*, **6**, 234 (1930); RUBBER CHEMISTRY AND TECHNOLOGY, **4**, 75 (1931).

[6] Stillwell, *Ind. Eng. Chem.*, **23**, 703 (1931).

[7] Stillwell and Clark, *Ibid.*, **23**, 706 (1931).

[8] Staudinger, *Berichte*, **63**, 927 (1927).

[9] Dean, *Trans. Inst. Rubber Industry*, **8**, 25 (1932); RUBBER CHEMISTRY AND TECHNOLOGY, **6**, 76 (1933).

[10] Meyer and Mark, *loc. cit.*, p. 205.

[Translated for Rubber Chemistry and Technology from Kautschuk, Vol. 9, No. 11, page 172, November, 1933.]

Influence of Vulcanization on the Index of Refraction of Rubber

F. Kirchhof

Only recently McPherson[1] has measured various physical properties of highly purified raw rubber, among them its index of refraction. In this work McPherson obtained essentially the same values as did the present writer.[2] In the work of the latter it was pointed out that the sulfur of vulcanization has an influence on the index of refraction, because the high index of refraction of sulfur has a noticeable effect even at low degrees of vulcanization. As a result of other investigations, the present author has not until the present time carried on any further the work planned at that time. It was therefore a pleasure to find that McPherson had carried out these investigations with rubber purified by the process developed in his earlier experiments.

In the present work, the determinations of the index of refraction were made at 25° with an Abbé refractometer, and the method of total reflection was used. The rubber used for preparing the samples was free of protein and so-called rubber resins, and contained 99.5 per cent of pure rubber hydrocarbon. The samples were vulcanized to a stage where practically all of the sulfur added had combined with the rubber.

The results shown below were obtained with mixtures containing up to 12 per cent of combined S. A few of the determinations were made on mixtures with a higher sulfur content, but with these mixtures difficulties in the measurements were encountered. The measurements are summarized in the following table.

INDEXES OF REFRACTION OF RUBBER–SULFUR MIXTURES

Combined Sulfur		Index of Refraction at 25°	
Percentage by Weight (Based on the Rubber)	Atoms of Sulfur per C_5H_8 Group	Observed	Calculated from the Empirical Equation
0	0	1.5194	1.5190
2	0.043	1.5255	1.5258
4	0.089	1.5327	1.5330
6	0.136	1.5403	1.5405
8	0.185	1.5483	1.5482
10	0.237	1.5555	1.5564
12	0.290	1.5659	1.5648

The quantities of sulfur in the Table are based both on the percentage by weight combined with the rubber and on the number of atoms of sulfur per C_5H_8 group. If the index of refraction is expressed as a function of the atomic percentage of combined sulfur, the relation is, within the experimental error, a linear one. The empirical equation which expresses this relation is as follows:

$$n_D^{25} = 1.5190 + 0.158S,$$

where S is the atomic percentage of sulfur per isoprene group of the rubber. It shows therefore that the index of refraction of a vulcanizate with S atoms of sulfur per C_5H_8 group at 25°, referred to sodium light, is the same as the index of refraction of raw rubber (1.5190) increased by the product of the empirical factor

0.158 and the particular sulfur content, expressed as a fraction of one atom of sulfur per isoprene group.

This method appears to be suitable in the case of transparent rubber mixtures as a means of following the progress of vulcanization, and ascertaining quickly by physical methods when a definite state of vulcanization has been reached, provided that in each case acetone-soluble components (fatty acids, oils, etc.) and free sulfur are previously removed by acetone extraction.

References

[1] *Bureau of Standards Journal of Research*, **8**, 751 (1932); RUBBER CHEMISTRY AND TECHNOLOGY, **5**, 523 (1932).

[2] Kirchhof, *Kautschuk*, **8**, 137 (1932); RUBBER CHEMISTRY AND TECHNOLOGY, **6**, 92 (1933).

[Translated for Rubber Chemistry and Technology by K. Kitsuta from the Journal of the Society of Rubber Industry, Japan, Vol. 7, No. 3, pages 154–161, March, 1934.]

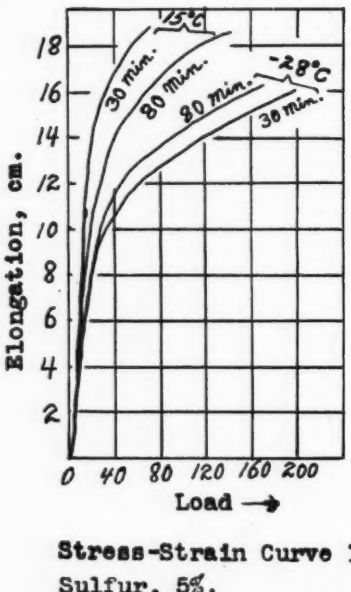
Characteristic Properties of Rubber at Low Temperatures. A Discussion of the Stress-Strain Curves of Vulcanized Rubber at Low Temperatures

Takeo Fujiwara and Toramatsu Tanaka

Introduction

The hardening of rubber at low temperatures is one of the well-known physical characteristics of rubber.

The loss of elasticity of raw rubber by hardening at 0° to 10° C., its turning to the consistency of glass, and its fragility at −19° C. when cooled with liquid air, and its fibering when stretched to 60–70 per cent previous to breaking, give an experimental proof of the theory of the structure of rubber molecules.



Stress-Strain Curve 1
Sulfur, 5%.
Vulcanized 30 and 80 min.

Figure 1

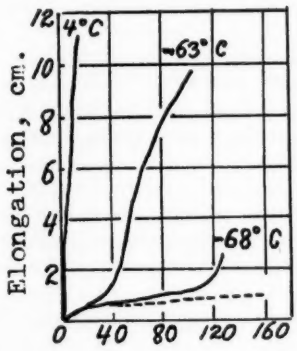
Vulcanization makes raw rubber physically less sensitive to heat and to low temperatures, and is of great significance, because it enables vulcanized rubber to be used around −30° C. without losing its elasticity. The effect of external heat on the physical properties, especially on the stress-strain relations, of vulcanized rubber has been discussed mainly for temperatures from −10° to +100° C., and only two papers deal with temperatures from −30° to −60° or −70° C. (cf. Le Blanc and Kröger, *Kolloid Z.*, **37**, 205 (1925); Tener, Kingsbury and Holt, *Bureau of Standards Technologic Papers*, Vol. **22**, No. 364).

Of special importance are a means of recognizing changes in the physical properties (phenomenon of freezing-hardness) of vulcanized rubber at −30° to −60° or −70° C., and the practical value of such information.

Though there is a contradiction in the fundamental meaning of the "cold-resistant theory" of rubber, investigations of the two phases of the subject may throw some light on practical problems and widen the scientific point of view.

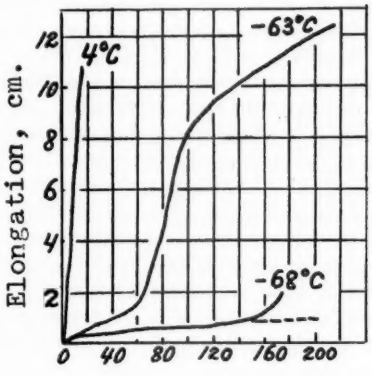
It seemed convenient to study the requirements for rubber products which are intended for use at low temperatures around −40° to −50° C. from three points of view: (1) the suitability or unsuitability of the products for cold-resistant

purposes; (2) the stability of vulcanized rubbers for continuous use at low temperatures; (3) the measurement of the true mechanical properties of vulcanized rubber at low temperatures, and its practical value.



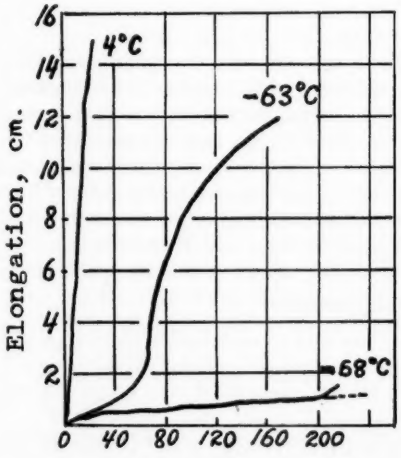
Load
Stress-Strain Curve 2
Sulfur, 2%
Vulcanized 80 min.

Figure 2



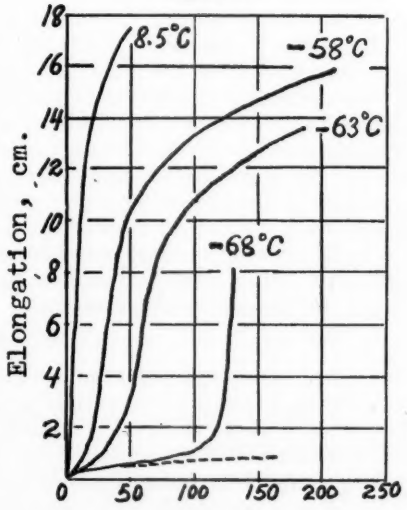
Load
Stress-Strain Curve 4
Sulfur, 2%
Vulcanized 160 min.

Figure 4



Load
Stress-Strain Curve 3
Sulfur, 2%
Vulcanized 120 min.

Figure 3



Load
Stress-Strain Curve 5
Sulfur, 5%
Vulcanized 40 min.

Figure 5

These three features are closely related to one another, and, though an ideal rubber should fulfil all requirements for some purposes, one feature may be of

special importance. For instance, rubber boots used in a cold climate are made by adding more vaseline(?) or reclaimed rubber than is present in the ordinary type of mixture in order to give a softer texture when the rubber itself freezes, and this will give an apparent improvement. It is generally believed that rubbers which have been frozen once recover their original properties on warming. In some cases, however, products which had been chilled to −40° C. (or even at 0° to −4° C.) for three months, or even for one week, became useless when warmed. This is an especially important problem, and it should be studied in connection with the subject of aging during cold-treatment. Since rubber products show varying freezing phenomena, products which must be especially elastic should be measured for their limit of elasticity at low temperatures.

These facts indicate that the development of an ideal rubber for cold-resistance is a very difficult task, and there is no other way than to attack each individual problem after careful analysis of its complex phases. Another important problem is to investigate how far the present approved method for testing cold-resistant rubber is in agreement with fundamental principles.

The object of this paper is to discuss the problem in an introductory way. The experiments which are described show that vulcanized rubber gives unexpected stress-strain curves at low temperatures.

EXPERIMENTS AND DISCUSSION

Apparatus and Manipulation

The object of this experiment, as mentioned above, was to determine the stress-strain curves of vulcanized rubber at low temperatures. The constant low-temperature apparatus which was found suitable for this experiment has been described by Matsui and Kambara (cf. *J. Soc. Rubber Ind., Japan*, **7**, 162 (1934)).

The samples consisted of small rings with 1.2-cm. inner diameter, 0.1-cm. thickness, and 1.7-cm. outside diameter. They were vulcanized in a press.

The mechanical strength and the elongation were measured by reading the position of a wire which was attached to the sample in the low temperature apparatus. The lower end of the wire was attached to a box containing iron rods (approximately 239 grams) for loading. These were added at the rate of one rod each 5 seconds. Readings were made by noting the position of a point on the wire on the scale. Corrections for elongation of the wire by the load were also made. The mechanical strength of the rubber was determined by the number of iron rods (or in grams). The elongation was measured in percentage. This technic was very simple, but was sufficiently accurate.

1. Preliminary Experiment

A sample was prepared by compounding 5 per cent of sulfur with pale crepe and vulcanizing in steam at 60 pounds' pressure per square inch for 60 minutes. A test at room temperature (15° C.) showed a tensile strength of 59.6 kg. per sq. cm. and an elongation of 895 per cent.

The results of the tests after keeping at low temperatures (−28° C.) for 30, 60, 120, 180, and 300 minutes are indicated in Table I.

TABLE I

Time of Treatment (Min.)	Tensile Strength (Kg. per Sq. Cm.)	Elongation (Percentage)
30	111.3	760
60	108.5	765
120	140.0	790
180	142.8	810
300	116.2	770

(Average value of 3 to 8 samples)

There are practically no differences in the results of cold treatment from 30 minutes to 5 hours. In general, the samples lost about 10 per cent of their elongation and increased about 120 per cent in tensile strength.

Though Holt has reported that 5 or 10 minutes' cold treatment is sufficient, all samples tested hereafter were chilled for one hour to have a factor of safety.

2. The Relation between the Conditions of Vulcanization and the Change of Mechanical Strength by Cold Treatment around −30° C.

As stated in the introduction, it is the general belief that there is practically no loss in elasticity when rubber is cooled to −30° C. Our preliminary experiment showed, however, some freezing effect and some changes in tensile strength and elongation. Therefore the relation between the conditions of vulcanization and the degree of freezing around −30° C. was studied.

Samples were prepared by compounding 5 per cent of sulfur and vulcanizing by steam at 60 pounds' pressure per square inch for 30, 50, 70, 80, 100, and 130 minutes. The tensile strengths and elongations of the samples kept at 15° and −28° C. are given in Table II.

TABLE II

Time of Vulcanization (Min.)	Tensile Strength (Kg. per Sq. Cm.)		Elongation (Percentage)	
	15° C.	−28° C.	15° C.	−28° C.
30	47.6	139.0	890	728
50	80.5	135.8	840	758
70	86.1	119.0	850	767
80	86.8	117.6	855	743
100	76.3	91.2	830	717
130	74.9	67.0	780	675

The lower the state of vulcanization, the greater was the increase in tensile strength when the samples were chilled. The changes in tensile strength and elongation of the optimum-vulcanized sample were not great enough to impair the quality for practical use. The stress-strain curve had nearly the same trend as for an ideal elastic substance, though it had a slight tendency to approach the stress axis.

The greater hardening effect by freezing in the case of the lower-vulcanized samples indicates that vulcanization causes rubber to become less sensitive to heat and to cold. It is however unwise to draw the conclusion from this experiment that cold-resistant rubber can be obtained by overvulcanization; the only statement that can be made here is that the treatment around −30° C. brought about no significant change in the stress-strain curve.

3. Stress-Strain Curves of Vulcanized Rubbers around −60° C.

The changes in the tensile strength and elongation of vulcanized rubber at low temperatures are well known, and are indicated in Experiments 1 and 2. There is, however, no record of experiments on stress-strain curves around −60° C. Though Holt stated that rubber shows a peculiar behavior around −60° C. or lower, he did not show any curves.

Since determinations of tensile strength and elongation alone do not reveal the true physical properties of rubber, stress-strain curves were made, while at the same time the tensile strengths and elongations were obtained.

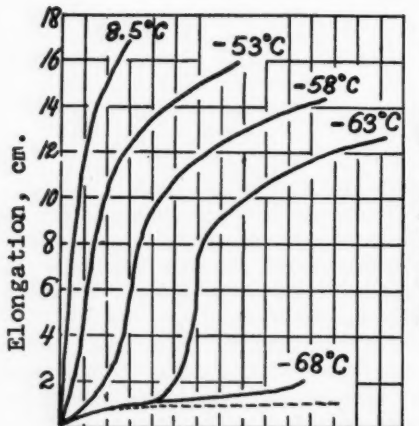
Samples were prepared by compounding 2, 5, and 8 per cent of sulfur and vulcanizing by steam at 60 pounds per square inch for 80, 120, and 160 minutes for 2 per cent of sulfur, 40, 80, 120, and 160 minutes with 5 per cent of sulfur, and 40, 80,

and 120 minutes with 8 per cent of sulfur. The tensile strengths and elongations of the samples treated at −58° C. and −63° C. are given in Table III.

TABLE III

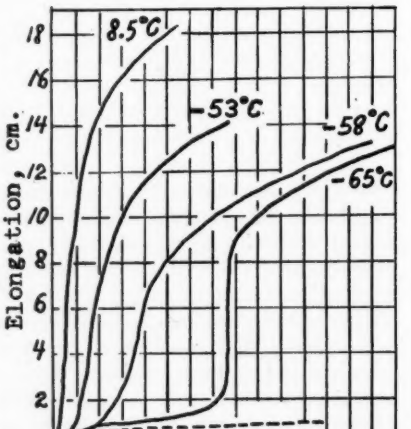
Sulfur (Percentage)	Time of Vulcanization (Min.)	Tensile Strength (Kg. per Sq. Cm.)			Elongation (Percentage)		
		8.5° C.	−58° C.	−63° C.	8.5° C.	−58° C.	−63° C.
2	80	9.8	...	70.7	540	...	450
2	120	15.6	...	119.0	722	...	555
2	160	10.5	...	147.0	523	...	565
5	40	34.8	146.3	129.5	843	745	635
5	80	47.8	162.4	200.2+	830	680	605+
5	120	76.7	196.0	207.9	880	610	620
5	160	68.8	121.1	177.8	825	50	20
8	40	54.1	139.3	144.2	717	700	610
8	80	82.6	207.2	155.4	770	515	45
8	120	79.8	172.9	...	678	35	...

These curves differed greatly from the usual stress-strain curves of rubber in that (1) the curves showed two distinct points of inflection, and (2) the elongation did not increase with increasing load. In the former case, the elongation was less



Load
Stress-Strain Curve 6
Sulfur, 5%
Vulcanized 80 min.

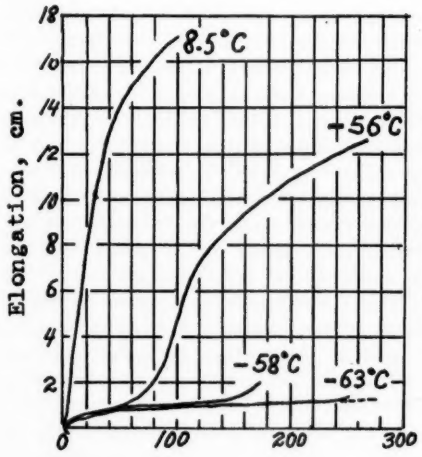
Figure 6



Load
Stress-Strain Curve 7
Sulfur, 5%
Vulcanized 120 min.

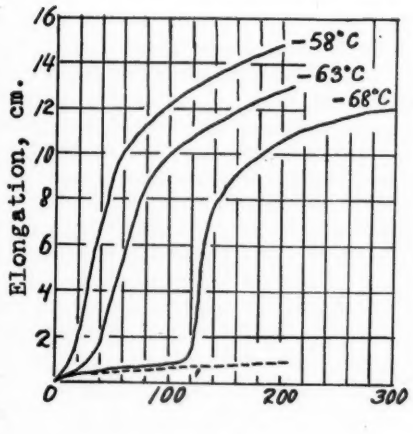
Figure 7

at the initial stress, and then increased suddenly when the stress reached a certain value, after which the elongation decreased with more loading up to rupture. This may be due to an accumulation of internal heat produced by stretching at the initial period, which makes possible a subsequent sudden elongation; the curve then became normal as a result of the internal heat produced by the sudden elongation. In the latter case insufficient internal heat was produced by stretching, with the



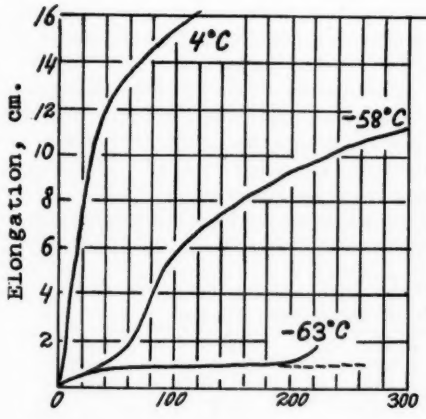
Load
Stress-Strain Curve 8
Sulfur, 5%
Vulcanized 160 min.

Figure 8



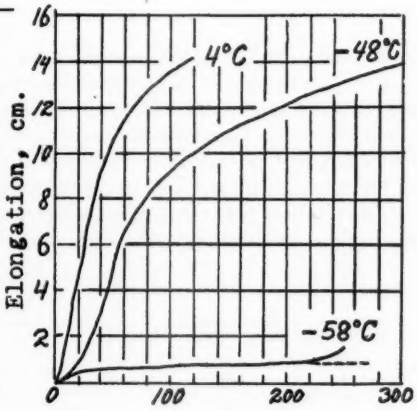
Load
Stress-Strain Curve 9
Sulfur, 8%
Vulcanized 40 min.

Figure 9



Load
Stress-Strain Curve 10
Sulfur, 8%
Vulcanized 80 min.

Figure 10



Load
Stress-Strain Curve 11
Sulfur, 8%
Vulcanized 120 min.

Figure 11

Remarks on stress-strain curves: the load is indicated by the numbers of iron sticks added; dotted lines indicate the elongation of wire itself by the load.

result that hard-freezing took place. The forms of the curves for the same low temperature treatment varied with the conditions of vulcanization. As shown in the diagrams, the greater the degree of vulcanization, the greater was the initial hardness on freezing. This may be related to the fact found by one of the authors that the Joule heat effect decreased with increase in the degree of vulcanization. Where the curve became normal by the effect of internal heat in the later period of loading, the tensile strength of the optimum-vulcanized sample was greater around −60° C., and this effect was far greater than around −30° C. Therefore in discussions of cold treatment, two types should be distinguished: those which show normal curves from the initial period of loading and those which show unusual curves at still lower temperatures.

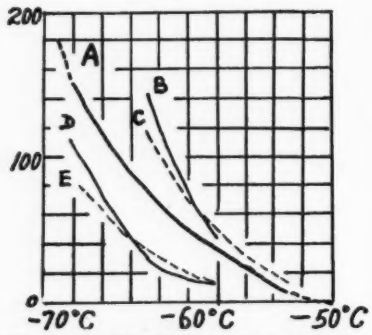


Figure 12—The Relation between the Temperature and Freezing-Hardness

Curve A, 5% sulfur and 80 min. vulcanization; B, 8% sulfur and 80 min. vulcanization; C, 5% sulfur and 120 min. vulcanization; D, 8% sulfur and 40 min. vulcanization; E, 2% sulfur and 80 min. vulcanization.

When a sample shows a normal curve for elastic rubber, it is safe to conclude that the sample is satisfactory for practical purposes, but if the curve has a kinked form, the rubber is unsuitable for practical uses, in so far as its elasticity is concerned. It is thus obvious that determinations of tensile strength and elongation alone do not give sufficient information about the physical properties of cold-treated rubber.

4. Cold Treatment of Vulcanized Rubber

Studies of the forms of curves indicated that the relation between the degree of vulcanization and the degree of cold-treatment is very complicated; a difference of 5° around −60° C. made great changes in the forms of the curves.

In order to obtain the limit of loading on the curve where a sudden elongation appeared after an initial freezing state, a tangent was drawn to the curve, and the point where the tangent and the elongation of the dotted line (elongation of wire by the load) met is called the freezing-hardness of vulcanized rubber. (The degree of hardness is expressed by using the numericals on the stress axis.)

The relation between the conditions of vulcanization and the freezing-hardness by various low temperature treatments is shown in Table IV and in Figure 12.

TABLE IV

Sulfur (Percentage)	Temperature (° C.)	Time of Vulcanization (Minutes) 40	80	120	160
2	−63	...	31.5	46.9	49.7
2	−68	...	85.4	147.0	122.5
5	−53	...	9.8	15.4	...
5	−58	14.0	28.7	43.4	119.0
5	−63	30.8	75.6	117.6	176.4
5	−68	83.3	147.0	...	...
8	−48	...	...	17.5	...
8	−58	14.0	44.8	170.8	...
8	−63	28.0	148.4	...	...
8	−68	112.0	...	...	...

Figure 12 shows that the lower the temperature, the greater is the freezing-hardness. For a given temperature of treatment, the freezing-hardness increases

with increase in the time of vulcanization. When the time of vulcanization and the temperature of cold-treatment are the same, the freezing-hardness increases with an increase in the percentage of sulfur.

Judged by the curves in Figure 12, there was no initial freezing above −50° C., whereas the samples became inelastic at −60° to 70° C., and showed permanent freezing.

Though it is sometimes said that vulcanized rubber is cold-resistant down to −50° C., this seems to be a case of the absence of an initial freezing-hardness.

From these facts, the conclusion is reached that the fundamental requirement for cold-resistant rubber is a zero freezing-hardness at the desired low temperature. In other words, it is of the greatest importance, in the manufacture of cold-resistant rubber, to use less sulfur and to shorten the time of vulcanization in order to prevent the mechanical and thermal destruction of the rubber molecules.

The experiments were carried out in the Laboratory of Applied Chemistry in the Tokyo Engineering College, and thanks are due to Dr. Y. Tanaka for his kindly advice and to Dr. G. Matsui and Mr. S. Kambara for help in the construction of the apparatus.

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The Action of Copper Salts on Raw Rubber

B. V. Buizov, V. S. Molodenskii and N. I. Mikhailov

RUBBER LABORATORY OF THE CHEMICAL-TECHNOLOGICAL INSTITUTE OF LENINGRAD, U. S. S. R.

Publications by many authors have been devoted to the problem of the destructive effect of copper salts and salts of other heavy metals on rubber.[1] The result of all these investigations can be summarized by the statement that copper salts as well as the salts of other heavy metals can be regarded as very active accelerators which bring about the autoöxidation of rubber, the rubber being changed irreversibly and in most cases being destroyed.

The evidence of these investigators does not make it possible to draw any definite conclusions with respect to the destructive action of the heavy metal salts, such as those of copper, upon raw rubber, and as a matter of fact there is good reason for believing that the investigations point to another explanation of the nature of this interesting problem. Actually it is doubtful whether a heavy metal salt in rubber functions as a direct activator of molecular oxygen, in other words as an oxygen carrier.

The experimental results which appear in the literature lead us to believe that the process is a very complicated one, and for this reason it was decided to divide it into its individual partial processes. It was assumed that in the first stage of the process of the destructive action of the salts of heavy metals a disaggregation of the micelles takes place; this disaggregation leads to a considerable increase in the number of the free double bonds, and it is possible that atmospheric oxygen may take part to a considerable extent.

The destructive action takes place, we believe, only when the first stage has been passed. Nevertheless the causes of this destructive action are of direct interest to us, for by recognizing these causes, there is a greater possibility of combatting the action.

The material to be found in the literature does not however confirm this theory, though there are no facts which contradict it. Such a state of affairs induced us to carry out a series of experiments which would confirm our supposition completely.

Our experiments dealt first of all with the action of copper salts: (1) on rubber solutions; (2) on raw rubber as such, and (3) on the vulcanization process.

The Action of Copper Salts on Benzene Solutions of Rubber

A smoked sheet solution in benzene was used for the experiment. The benzene was treated for a long time with water-free sodium sulfate and distilled over metallic sodium. Copper oleate was chosen as the copper salt, perhaps the only copper salt which is soluble in benzene. As a method of investigation, the determination of the structural viscosity was selected.[2,3] The constants K and N of the de Wael-Ostwald equation were the values chosen to characterize the state of solution. In general the unknown factor S was utilized, where

$$S = \int_0^{P_{\eta\infty}} KP^{1-n}\,dP - P_{\eta,\eta\infty} = \frac{KP_{\eta\infty}^{2-n}\,(n-1)}{2-n}$$

$P_{\eta\infty}$ represents that pressure at which the relative viscosity of the colloid leaves the structural range and enters the simple range and $\eta\infty$ is the simple relative viscosity of the solution tested, which at pressures $P_{\eta\infty}$ follows the Hagen-Poiseuille law.

With this formula it is easy to show that the value S represents quantitatively the deviation of the particular colloid solution from the Hagen-Poiseuille law. This deviation is due to a definite structure of the colloid. Accordingly S represents the structural state of the rubber. It is equal to zero in the case of true solutions, and reaches very high values[4] in the case of lyophilic colloid solutions.

To the benzene solution was added a solution of copper oleate of different concentrations, likewise in benzene. Measurements of the structural viscosity were then made periodically over a long time. The results obtained are given in Table I, and are shown graphically in Fig. 1.

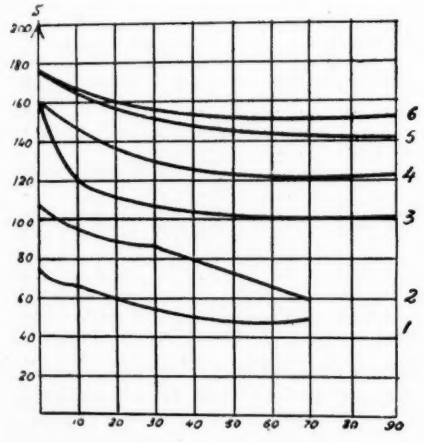

Figure 1

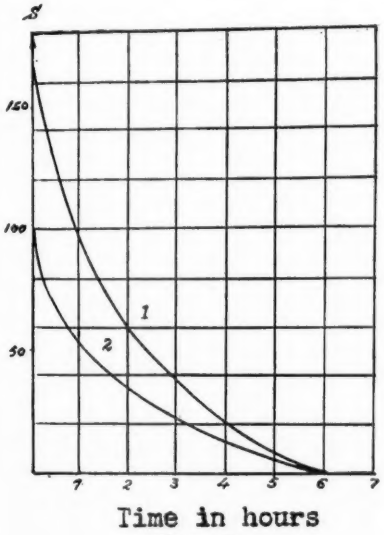

Figure 2

It is evident from this Table that the addition of even so small a quantity of copper oleate as 0.005 per cent exerts an appreciable effect. These changes in the structure of the solution which are brought about by the copper oleate become considerably greater as the copper oleate is added in increasing quantities to the solutions, *e. g.*, 0.005, 0.05, and 0.5 per cent. When such quantities of copper oleate are added to rubber solutions, a very strongly marked structural change takes place immediately and the factor S diminishes, *i. e.*, the structure of the colloid is destroyed. After a short time the curve changes its course and becomes almost parallel to the abscissa. At the end of 30 days for a rubber solution containing 0.005 per cent of copper oleate and at the end of 10 days in the case of one with 0.5 per cent, appreciable kinks in the curves are evident. The value S again diminishes abruptly and once more approaches the abscissa. This break in the curve is found only when the quantity of copper salt amounts to at least 0.01 per cent, and it always occurs under these conditions. With smaller quantities the break is not so distinct.

The results of Table I can probably be used to explain the structural change in rubber in solution. We are inclined to feel that the entire process can be divided

TABLE I

PERCENTAGE OF COPPER (IN THE FORM OF OLEATE) BASED ON THE VOLUME OF RUBBER SOLUTION

Time in Days	1 0.5%			2 0.05%			3 0.005%		
	K	n	S	K	n	S	K	n	S
0	16.2	1.219	165	16.2	1.219	165	16.2	1.219	165
2	..	...	...	10.5	1.191	103	12.8	1.203	128
4	..	...	...	..	...	...	..	...	...
7	8.8	1.175	83	..	...	...	..	...	...
10	..	...	...	..	...	...	..	...	...
13	..	...	...	9.4	1.174	89	..	...	...
17	7.2	1.136	61	..	...	...	..	...	...
19	..	...	...	9.3	1.174	88	11.8	1.200	121
40	6.6	1.133	55	..	...	...	..	...	...
49	..	...	...	8.0	1.151	71	11.1	1.182	109
68	5.9	1.115	45	7.1	1.124	57	..	...	...
83	..	...	...	..	...	...	10.3	1.180	99

Time in Days	4 0.0005%			5 0.00005%			6 Control Solution		
	K	n	S	K	n	S	K	n	S
0	16.2	1.219	165	16.2	1.219	165	16.2	1.219	165
2	..	...	...	..	...	...	..	...	...
4	15.1	1.217	153	..	...	...	..	...	...
7	..	...	...	..	...	...	..	...	...
10	14.2	1.213	144	..	...	...	15.5	1.218	158
13	..	...	...	..	...	...	..	...	...
17	..	...	...	..	...	...	..	...	...
19	13.1	1.207	129	14.6	1.216	149	15.0	1.217	153
40	..	...	...	..	...	...	..	...	...
49	12.3	1.200	123	14.1	1.214	145	..	...	...
68	..	...	...	..	...	...	..	...	...
83	12.0	1.195	120	14.1	1.214	145	14.9	1.216	152

into three stages. Copper oleate brings about a desolvation of the rubber micelles. In this way the structural viscosity is reduced actively and to a considerable extent. This stage is of short duration, *i. e.*, a matter of minutes, and the structural viscosity then diminishes much more slowly. Here a micellar disaggregation apparently occurs, *i. e.*, the aggregates of rubber micelles break up into smaller aggregates. Molecular disaggregation begins at a time which corresponds to the break in the curve. Here a breakdown of the rubber micelles takes place. Such an explanation is in complete agreement with the observations and conclusions of Bary, who arrived at the same result in a study of aging phenomena at high temperature, in fact he mentions micellar and molecular disaggregation.[5]

The following results have confirmed the hypothesis which we have advanced. A 0.477 per cent rubber solution (smoked sheet) in benzene with 0.5 per cent of copper oleate was exposed to ultra-violet radiation. At the same time a parallel experiment was carried out in which the same rubber solution without copper oleate received the same treatment. The exposure was for 6 hours (see Table II and Fig. 2).

TABLE II

Time of Irradiation	A 0.477 Per Cent Benzene Solution			The Same Solution + 5 Per Cent of Copper Oleate		
	K	n	S	K	n	S
0	16.2	1.219	165	16.2	1.219	165
1	8.68	1.168	81	5.31	1.104	38
3	3.16	1.060	17	2.87	1.048	12
6	2.00	1.00	0	1.74	1.00	0

Within 6 hours the S value dropped from 165 to 0. Upon still further irradiation no change in the rubber solution could be found. The value K remained constant.

Table II indicates that the value K of the control sample approached that of the sample containing the copper salt (2.00 *versus* 1.74); still it should be observed that the K value of the rubber solution containing copper oleate was somewhat smaller. We believe therefore that, where the result of the process in both experiments is the same, K should have the same value in both experiments. Although the difference is very slight, the diminution in the K value of the rubber solution containing copper oleate within the entire range of decrease in the concentration of rubber can be attributed to the formation of a flocculent precipitate in the benzene solution.[6]

TABLE III

Time in Hours	1 Control Solution (Rubber Alone)			2 1% Copper Oleate			3 1% of Accelerator A*			4 1% of Trinitrotoluene		
	K	n	S	K	n	S	K	n	S	K	n	S
0	14.8	1.210	148	14.8	1.210	148	14.8	1.210	148	14.8	1.210	148
2	14.8	1.210	148	11.6	1.200	116	15.6	1.234	166	16.2	1.231	168
8	14.8	1.210	148	10.3	1.181	99	14.2	1.207	140	15.9	1.227	165
50	14.8	1.210	148	8.95	1.168	83	13.2	1.206	133	15.9	1.227	165

Time in Hours	5 1% Copper Oleate + 1% Trinitrotoluene			6 1% Copper Oleate + 1% Trinitrotoluene			7 1% A* + 1% Trinitrotoluene			8 1% Copper Oleate + 5% A* + 5% Trinitrotoluene		
	K	n	S	K	n	S	K	n	S	K	n	S
0	14.8	1.210	148	14.8	1.210	148	14.8	1.210	148	14.8	1.210	148
2	10.9	1.181	107	11.2	1.191	110	14.7	1.217	150	10.2	1.180	98
8	10.7	1.179	104	10.1	1.171	94	14.0	1.211	142	9.67	1.169	90
50	10.3	1.146	90	8.87	1.168	81	13.7	1.210	138	8.28	1.150	74

* A = anhydroformaldehyde.

If therefore the diminution in the concentration of rubber in the presence of the copper salt is taken into consideration, it is found that the K values of the two solutions are identical. It may be concluded from this that the destruction of the rubber molecule by the action of ultra-violet radiation and by the copper salt is the same as by irradiation alone. The copper salts accelerate only this decomposition, particularly in the first stage of the process; such salts bring about a desolvation of the rubber micelle. This effect takes place immediately after addition of the copper salt, and therefore before any actual irradiation.

TABLE IV

Time in Hours	1 Control Solution (Rubber Alone)			2 1% Copper Oleate			3 1% Benzoyl Peroxide		
	K	n	S	K	n	S	K	n	S
0	100.6	1.340	1082	100.6	1.340	1082	100.6	1.340	1082
2	...	...	..	58.8	1.309	634	100.5	1.367	1080
50	...	...	..	46.5	1.258	493	...	...	..
75	...	...	..	...	...	..	51.8	1.254	548
200	...	...	..	44.4	1.247	436	27.0	1.192	265
360	96.4	1.337	1041	38.1	1.238	397	14.5	1.129	118

Time in Hours	4 1% Benzoylperoxide + 1% Copper Oleate			5 1% Aluminum Oleate			6 1% Iron Oleate		
	K	n	S	K	n	S	K	n	S
0	100.6	1.340	1082	100.6	1.340	1082	100.6	1.340	1082
2	37.3	1.241	390	63.0	1.300	678	72.1	1.308	777
50	14.4	1.132	119	...	...	....	...	...	....
75	11.8	1.100	83	...	...	....	...	...	....
200	7.18	1.066	37.5	...	...	....	...	...	....
360	4.65	1.047	18.5	630(?)	1.300	67.8	72.1	1.308	77(?)

Very interesting results were also obtained in a study of the action of other agents, including trinitrotoluene as an oxidizing agent, anhydroformaldehyde-aniline as a reducing agent, and a mixture consisting of each of the substances mentioned with copper oleate.

In this connection, special attention is called to the behavior of trinitrotoluene, which lowers to a slight extent the viscosity at the pressures ordinarily used in the Ostwald viscosimeter. However because of a distinct increase in N, the value of S also increases, which indicates that, within the 50 hours during which the experiment lasted, trinitrotoluene increased the degree of structure of the rubber. Anhydroformaldehyde-aniline increased at first the degree of structure of the rubber solution, but after 6 hours the S value diminished. The net result of the action was different when trinitrotoluene and anhydroformaldehyde-aniline were present together with the copper salt in the solution. The lowering is somewhat arrested by both agents, but not to the corresponding extent that trinitrotoluene alone in the absence of copper oleate increases the degree of structure. After 50 hours,

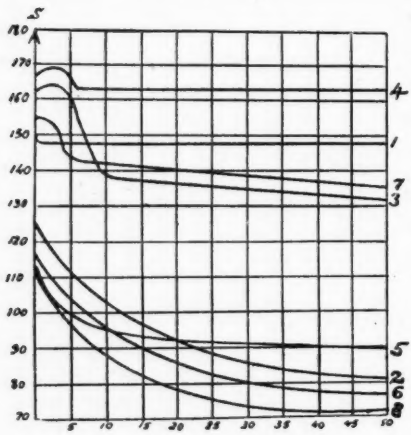

Figure 3

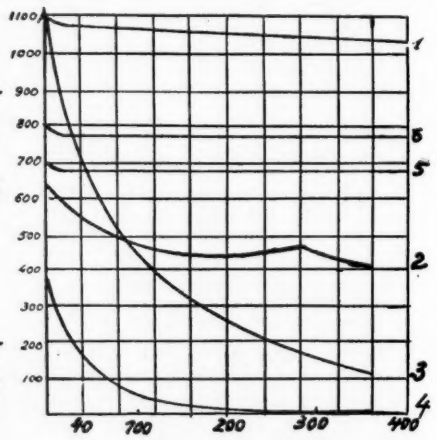

Figure 4

values are obtained, both for a solution containing copper oleate as well as for a solution containing trinitrotoluene and copper oleate, which indicated an identical structure in the two cases. Figure 3 shows clearly the tendency of the mixture of trinitrotoluene and copper oleate after 50 hours' action to decrease the degree of structure considerably (Curve 6), in fact to an extreme which is otherwise true only of copper oleate alone. The presence of all three agents, *i. e.*, trinitrotoluene, anhydroformaldehyde-aniline, and copper oleate together, in the solution has, even after only 15 hours, a far greater destructive effect on the rubber structure than would have occurred if the copper salt had been present alone (see Table III and Fig. 3).

These results confirm our opinion on the action of copper salts on rubber solutions.

Account must be taken of the fact that trinitrotoluene is only a mild oxidizing agent, which is not capable of oxidizing the rubber micelles. However, the copper salt makes possible an energetic oxidation by diminishing the solvation of the micelles and by starting disaggregation. The total surface area of the rubber

micelles is increased in this way. Likewise the surface energy becomes greater, which in turn promotes the reaction between trinitrotoluene and the rubber.

Our opinion was confirmed in a still more convincing way by the action of an even stronger oxidizing agent, *viz.*, by the action of benzoyl peroxide. In this experiment a one per cent solution of smoked sheet in benzene was used. Besides benzoyl peroxide, copper oleate, magnesium oleate, aluminum oleate, and iron oleate were also added to the solution (see Table IV and Fig. 4).

The curve which represents the change in structure of the rubber solution in the presence of copper oleate shows a kink at a point corresponding to a time of action of 280 hours. This break in the curve represents the transformation to a state of molecular disaggregation of the rubber. Curve 5 for aluminum, Curve 6 for iron, and Curve 7 for magnesium indicate only a desolvation of the rubber micelles

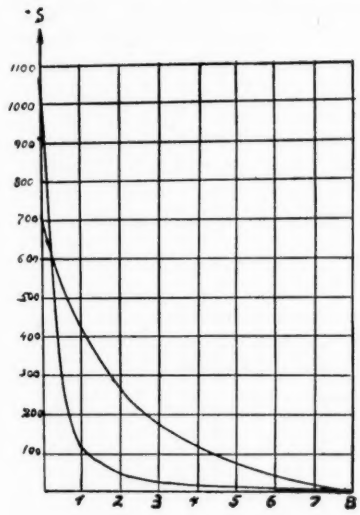

Figure 5

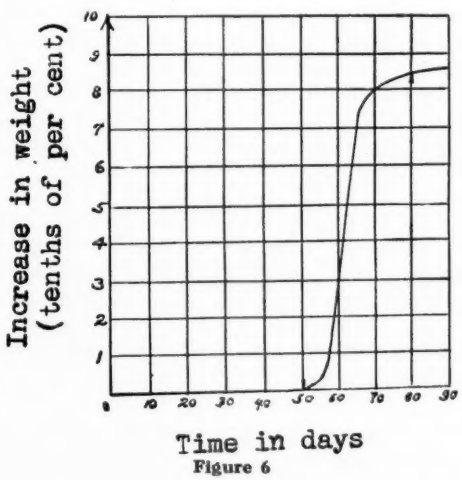

Figure 6

in the presence of the particular oleate; the structure of the micelles themselves is not attacked in any essential way.

The curve pertaining to benzoyl peroxide differs qualitatively from that pertaining to copper oleate. The curve has no steeply descending part in the initial stage of the action; it is evident that the change in the micellar structure of the rubber does not go further than the solvation. The benzoyl peroxide curve, as is to be expected, has no kink, and it probably represents the destructive process brought about by oxidation. Such a conclusion is still more comprehensible in view of further experiments described below. It is quite natural that Curve 4 (rubber + copper oleate + benzoyl peroxide) lies below Curve 2 (rubber + copper oleate). Here the micelles, disaggregated by the copper salt, undergo oxidation by benzoyl peroxide, an effect which is manifest in a fall of the curve to the abscissa and consequently in the structure. The curve has an almost straight course and has no kink. Curves 3 and 4 in Fig. 4 slope close to the abscissa, and the degree of structure is likewise almost zero. The *S* value of 397 after 360 hours is still rather high, and therefore the structure of the rubber micelles is still unattacked.

Probably the combined effect of both agents is necessary for the curve to approach the abscissa. To establish this time interval is of particular importance because when S is zero, K becomes constant. These factors alone make it possible to judge the nature of the decomposition products of the rubber. To accelerate the process, rubber solutions containing copper oleate were exposed for a long time to ultra-violet radiation (see Table V and Fig. 5).

With a copper salt present, the structure of the solution breaks down immediately after its preparation, as a result of desolvation. However if two rubber solutions, one containing benzoyl peroxide, the other containing copper oleate, are exposed to ultra-violet radiation, the benzoyl peroxide curve overtakes after a short time the copper oleate curve.

There are certain other facts which deserve mention. In the destruction of the rubber structure under the joint action of ultra-violet radiation and copper oleate (Solution I), the concentration of the rubber diminished as a result of the formation of a flocculent precipitate. On the other hand, a rubber solution which was exposed to ultra-violet radiation in the presence of benzoyl peroxide (Solution II) remained perfectly clear.[7] Now when S was zero, the K value of Solution II was considerably smaller than was the K value of Solution I. This difference in the K values can be explained only on the assumption that the decomposition products are different in the two cases. Such a natural consequence leads in turn to the conclusion that in the case of benzoyl peroxide oxidation products are formed, whereas in the case of copper oleate a far advanced disaggregation of the rubber micelles is involved.

TABLE V

ONE PER CENT SOLUTION OF SMOKED SHEET IN BENZENE

Hours of Irradiation	In the Presence of Copper Oleate			In the Presence of Benzoyl Peroxide		
	K	n	S	K	n	S
0	100.6	1.340	1082	100.6	1.340	1082
1	42.8	1.261	454	2.55	1.090	62.4
3	14.9	1.130	122	3.34	1.035	10.3
8	4.34	1.040	15.1	1.48	1.00	0

The S value diminishes, immediately after addition of the copper oleate, to a value of 670. For this reason Curve I falls below Curve 2, but after one-half hour Curve 2 has overtaken Curve 1.

The Action of Copper Salts on Raw Rubber

With the purpose of observing the changes which take place in rubber when copper salts are added, samples of raw rubber were prepared in various ways, as follows:

(1) Copper oleate was added to a solution of rubber in benzene, and the solvent was then evaporated to give the required films of rubber.

(2) Acetone was added to a rubber-copper oleate solution in benzene, and the rubber which separated was removed and dried.

(3) Latex was coagulated with cupric chloride solution, freed from serum, and the product dried.

(4) Various copper salts in powder form were milled into rubber.

The preparation and observation of the samples by the first three methods above were carried out both in the presence of air, and also in nitrogen, *i. e.*, practically in the absence of oxygen.

Observations on Rubber Films

The films prepared from the rubber solutions, as time went on, became tacky, or liquid, or softened greatly, and after a still longer time became vitreous and brittle. All these changes were observed in the course of the investigation, *viz.*, the appearance of tackiness, liquefaction, and brittleness.

In one of the numerous experiments, exactly 0.4 gram of smoked sheet was dissolved in 30 cc. of dry benzene, was let stand 5 days, and 0.0757 gram of copper oleate in benzene was then added. In a parallel blank experiment, 0.4 gram of smoked sheet was dissolved in benzene, and no copper salt was added. The solvent was evaporated, and after 2 days films were obtained. It should be mentioned that the film in the blank experiment retained tenaciously 1.1 per cent of solvent, whereas the films containing copper oleate immediately after being prepared, *i. e.*, after 2 days, weighed exactly the sum of the two components, *viz.*, 0.4 + 0.0757 gram. This phenomenon confirmed our opinion that copper oleate causes, in the first stage of the change, a desolvation of the rubber micelles. Table VI and Fig. 6 show that during the first 53 days there was no gain in weight of the films containing copper oleate. Nevertheless the films became tacky after 7 days, and turned into a viscous liquid mass after 53 days. From this stage on, there was a pronounced increase in weight, which continued for about one month, until a firm skin had formed on the surface of the film. It is worthy of note that the liquefaction of the film prepared in an atmosphere of nitrogen occurred after the same length of time as did that of the film prepared in air, *i. e.*, in the presence of oxygen. However no firm skin was formed on the surface of the viscous mass which was kept in nitrogen.

Particular attention should be paid to the fact that a fairly long time is required before there is any increase in weight. Only when extensive disaggregation has taken place does the rubber reach a state where it is able to absorb oxygen. This is evident not only in the experiments described above, but also in the experiment described below.

A 2.08 per cent solution of smoked sheet in benzene was exposed to ultra-violet radiation for 20 hours. At the end of these 20 hours, the structure of the rubber was completely destroyed, as is proved by the fact that the value S in the structure viscosity equation at the beginning of this article became equal to zero. Films were then prepared from this solution, and it was found that in an oxygen-free atmosphere the weight of the film corresponded to the original concentration of rubber. This meant that disaggregation of the rubber does not take place during an oxidation process. After lying in the laboratory for 24 hours, there was a gain in weight of 5.3 per cent. Films which had not been exposed to ultra-violet radiation showed gains in weight only after 2 months.

In a parallel experiment a similar solution of smoked sheet, to which however no copper oleate had been added, was exposed to ultra-violet radiation for 20 hours. In this case also, the structure-viscosity determination of the solution gave an S value of zero, whereas there was no increase in weight over a very long period of time. From this it may be concluded that on the one hand copper salts bring about a profound disaggregation without any accompanying oxidation, while on the other hand they act as catalysts of the autoöxidation of strongly disaggregated rubber. It is possible that the effect of copper salts is manifest in a change in the structure of the rubber in such a way that they appear to render the rubber chemically active.

Films which contained 1.1 and 30 per cent of benzoyl peroxide showed no tackiness after three months, for immediately after being prepared they became hard

and somewhat brittle. The effect of both agents, copper oleate and benzoyl peroxide, is characterized by the formation of tacky viscous films, on the surface of which a hard crust is formed after two or three days.

TABLE VI

Time in Days	Control Sample	Sample Containing Copper Oleate	Result
2	1.1	0	.....
8	1.1	0	Sticky film
53	1.1	0	
57	1.1	0.5	Films liquefied
60	1.1	3.4	
70	1.1	7.9	
80	1.1	8.6	Firm skins on the surfaces of the films
90	1.1	8.6	
100	1.1	8.6	

The numerous observations which were made on such rubber films warrant the conclusion that copper oleate brings about a desolvation in the initial stage, and this immediately promotes evaporation of the solvent. In the second stage, copper oleate brings about a disaggregation, which is manifest in the appearance of stickiness and a viscous liquid condition. In the final stage the completely destroyed rubber is oxidized by atmospheric oxygen, and this oxidation can be followed easily by the increase in weight and by the formation of a brittle crust.

Observations on a Sample of Rubber Precipitated with Acetone

The samples prepared as above were tacky immediately after their preparation, and after standing they became converted into viscous pasty liquids. This change took place both in air and in nitrogen. The experiments included measurements of the structure viscosities, surface tensions, indices of refraction, and light dispersion.[8] The structure viscosity measurements showed S values of zero. On the basis of this series of measurements, it was proved that after twenty days the samples kept in nitrogen were no different from those kept in air. The results were almost the same as those obtained with a cold-masticated rubber containing no copper salts. The only differences were in the values of the light dispersion of the samples containing copper oleate and the masticated ones, *viz.*:

$J = 10.5 \times 9.10^{-10}$ amp. for a one per cent solution of cold-masticated rubber.
$J = 5.0 \times 9.10^{-10}$ amp. for a one per cent solution of rubber containing copper oleate.

According to the Rayleigh equation, it is safe to assume that the rubber in the second solution has a much higher degree of dispersion. Our experiments on the determination of the solubility (rate of solution) according to the method of Miedel have confirmed this assumption. It is therefore quite possible that the changes in the rubber brought about by cold mastication are from a qualitative standpoint identical in many ways to those in rubber to which copper oleate has been added.[9]

Observations on a Rubber Obtained by Coagulation of Latex with Cupric Chloride

Among many results of observations of a rubber obtained by coagulation of latex with cupric chloride, one observation in particular should be mentioned. This sample, like the previous samples, had been stored for a long time in nitrogen as well as in air. In the case of a sample which had been prepared in an atmosphere practically free of oxygen, and which was then stored in air and also in nitro-

gen, the stickiness was manifest only in the interior. On the other hand the surface was covered with a firm skin. It may be assumed that the stickiness results from oxidation and is accelerated by the copper salt which is present. In this case the oxidation would have to spread from the outside toward the inside, particularly since the rubber was prepared in an atmosphere free of oxygen. However, we have quite a different picture of the phenomenon, which confirms our view that copper salts disaggregate rubber and thus bring about stickiness. Rubber disaggregated in this way is however easily subject to oxidation, as a result of which a firm skin is formed on the surface.

In this connection it should be noted that a sample prepared under normal conditions, *i. e.*, with air present, though it has undergone a superficial change, still possesses the same heat conductivity as that of a rubber sample to which no copper salt has been added.[10]

Observations on Rubber Samples to Which Copper Salts Had Been Added during Mastication

Cuprous and cupric chlorides, cupric acetate, cupric sulfide, and cupric oxide were added in powder form to rubber during mastication. The samples became dark brown immediately, and the cloudiness characteristic of masticated rubber became less. After seven or eight days a slight stickiness became evident on the samples prepared in this way, and after 3 to 4 months they began to liquefy. The surface, however, became covered with a firm skin. The structure viscosity, refraction and surface tension values of solutions of the rubber in benzene were not very different from those of the control samples to which no copper salt had been added, and which had been cold-masticated. Only in the rate of solution in ether was a difference manifest, where the rate was greater in the case of the rubber samples containing the copper salt.

The samples containing one per cent of the compounds mentioned above were placed in a drying oven at 85° C., and any increases or decreases in weight and any external changes were observed. The results are given in Table VII.

TABLE VII

INCREASE OR DECREASE IN THE ORIGINAL WEIGHT
(in Percentage)

Time in Hours	Control (Blank)	Cupric Sulfide	Cupric Oxide	Cupric Acetate	Cupric Chloride	Cuprous Chloride
2	−0.15	−0.15	−0.15	−0.36	−0.33	−0.41
7	−0.14	+0.22	−0.06	−1.03	−0.90	−0.58
14	−0.03	+0.32	+0.22	−0.98	−0.83	−0.55
25	+0.04	+0.35	+0.90	−0.92	−0.76	−0.51
72	+0.47	+0.66	+1.27	+0.05	+0.06	+0.06

After 72 hours the samples had changed in the following ways:

Control (blank)	somewhat sticky on the surface
Cupric sulfide	a brittle crust on the surface
Cupric oxide	a brittle crust on the surface
Cupric acetate	very sticky on the surface
Cupric chloride	elastic, non-sticky surface
Cuprous chloride	elastic, non-sticky surface

These results lead to the conclusion that the addition of water-soluble copper salts results in the formation of volatile compounds, with consequent losses in

weight. A chemical reaction also takes place between these compounds and the rubber. This is, however, not true of cupric sulfide and cupric oxide, for these accelerate the oxidation of rubber and bring about increases in weight. As a result of this oxidation a firm skin is formed on the surface, and this skin hinders the progress of the oxidation into the interior part of the rubber.

As mentioned above, rubber is converted by copper salts into a viscous liquid mass, with formation at the same time of a firm surface skin as a result of oxidation. The formation of this skin takes place very slowly under ordinary conditions. This process can, however, be accelerated considerably by an increase in temperature, and ultra-violet radiation likewise brings about the formation of a skin, which under these conditions remains very firmly attached to metal and glass.[11]

The Effect of Copper Salts on the Vulcanization Process

The properties of rubber are most plainly evident in the vulcanization process. This process offers therefore the best method for solving the problem as to what

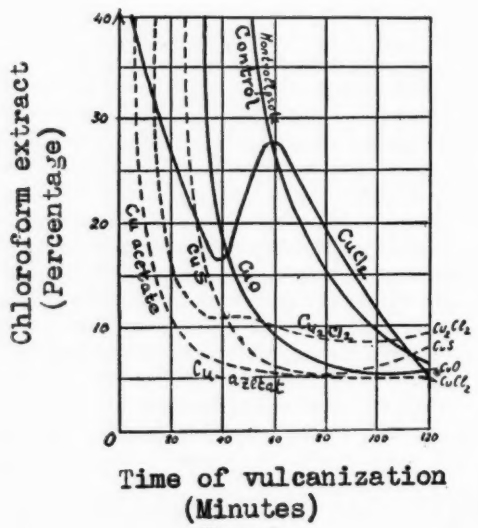

Figure 7

effect the salts of heavy metals have on rubber. Experiments on this subject are not yet finished, but a few results will be described in a preliminary way.

It was found that all the copper salts mentioned accelerate vulcanization, even when they are present in very small proportions, *i. e.*, from traces up to one per cent. They do not increase the combination of sulfur. For example, judged by the chloroform extracts, the optimum vulcanization of a mixture with 5 per cent of sulfur was 120 minutes. When 1 gram of copper in the form of compound was added to this same mixture, the optimum dropped to 30 minutes for cupric sulfide and to 60 minutes for cupric oxide. In these experiments the samples were vulcanized in steam at 143° C. The mixtures with cupric acetate, cupric sulfide, and cupric oxide showed the same minimum in their chloroform extracts at the optimum vulcanization as did the control sample (see Table VIII and Fig. 7).

TABLE VIII

Time of Vulcanization (in Minutes)	Chloroform Extract (in Per Cent × 10)					
	Control	Cupric Chloride	Cuprous Chloride	Cupric Acetate	Cupric Oxide	Cupric Sulfide
30	78.8	20.7	10.8	6.3	46.4	31.7
45	50.2	15.5	10.7	6.0	15.8	10.8
60	29.0	27.1	10.2	5.8	8.3	5.7
90	15.8	16.6	7.2	5.1	5.4	5.7
120	6.4	4.2	8.6	5.5	5.8	7.5

A mixture milled with any of the copper salts and then stored for 2 weeks lost to a great extent its ability to vulcanize.

For example, the following mixtures were prepared:

	(1)		(2)	
Smoked sheet	100		Smoked sheet	100
Sulfur	5		$CuCl_2.2H_2O$	2.68 (Cu 1)
$CuCl_2.2H_2O$	2.68 (Cu 1)			

These mixtures were kept for 2 weeks in the laboratory at ordinary room temperature, at the end of which time 5 parts of sulfur were added to the second

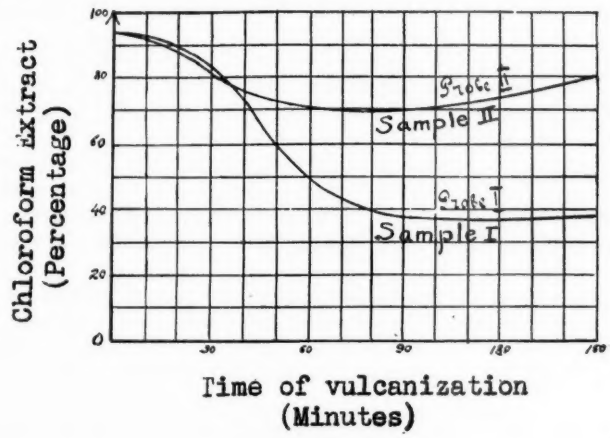

Figure 8

mixture. Both mixtures were then heated in steam at 143° C. The results are given in Table IX and in Fig. 8, and show that both samples lost to a large extent their capacity to vulcanize.

TABLE IX

Vulcanization Period in Minutes	Chloroform Extract (In per cent × 10)	
	Sample I	Sample II
30	82.2	81.4
45	72.0	69.0
60	48.5	61.6
90	40.4	59.4
120	41.9	60.7
180	35.1	72.4

In this connection one must not forget the fact that water-insoluble copper compounds are strong accelerators. The results indicate that in the first stage

copper compounds bring about changes in rubber which activate the latter in vulcanization. On the other hand if this initial stage is to be regarded as one step in the autoöxidation of rubber, then there would have to be an increased combination of sulfur. In this case the sulfur is analogous to oxygen. This is however not true, for copper accelerates vulcanization, probably however only the physical and not the chemical process. The fact that after two weeks rubber had lost its ability to vulcanize is explained by the progressive and extensive disaggregation, as a result of which the rubber structure is destroyed, independent of whether it has become oxidized or not.

Conclusions

1. An examination of the literature makes open to doubt the view of many investigators that copper salts exert a destructive action on rubber by functioning as catalysts which start the autoöxidation of rubber and then promote this autoöxidation. The literature available indicates with just as good reason that there is another explanation of the effect of copper salts, *viz.*, that the destructive action of these salts is characterized in its initial stage by a disaggregation of the rubber. As a result of this disaggregation there is an increased surface of rubber micelles with an accumulation of double bonds. The rubber is then more readily susceptible to oxidation by atmospheric oxygen.

2. The detailed study in the present work of the action of copper salts on rubber solutions has shown that the complicated process as a whole can be divided into separate partial processes, *i. e.*, into a desolvation, a micellar disaggregation, and a molecular disaggregation.

3. Observations of changes in weight and of the properties of rubber films proved conclusively that copper salts first bring about a desolvation of the rubber micelles and then a disaggregation. The latter proceeds without any accompanying oxidation of the rubber. Following this there is an oxidation of the irreversibly degenerated rubber.

4. The influence of oxygen on the appearance of stickiness is very slight, in fact tackiness appears both in the presence and the absence of oxygen.

5. The stickiness of rubber samples to which a copper salt has been added is always to be found in the interior of the samples, while a brittleness appears on the surfaces.

6. These facts lead to the conclusion that the stickiness of raw rubber appears as a result of disaggregation, whereas brittleness is the result of oxidation.

7. The destructive effect of copper salts depends to a large extent upon the state of dispersion of the copper salt in the rubber; the more finely dispersed is the salt in the rubber, the greater is its effect.

8. Copper salts accelerate vulcanization, without however increasing the proportion of combined sulfur. Upon standing a long time, rubber containing a copper salt loses completely its power of vulcanization. This latter phenomenon can be explained by the fact that copper compounds bring about in a relatively short time the disaggregation which is necessary to vulcanization, whereas after a longer time they destroy the rubber completely.

References

[1] A Compilation of the literature is to be found in the works of Dufraisse, *Rev. gén. caoutchouc*, **85**, 4 (1932); No. 86, 3 (1932); RUBBER CHEM. AND TECH., **6**, 157 (1933); and of Jones and Craig, *Ind. Eng. Chem.*, **23**, 23 (1932); RUBBER CHEM. AND TECH., **4**, 108 (1931). Special attention is also called to the works of Kirchhof, *Kautschuk*, **3**, 256 (1927) and of Freundlich and Talalay, *Kautschuk*, **9**, 34 (1933); RUBBER CHEM. AND TECH., **6**, 378 (1933).

[2] Our investigations on the effect of various metallic salts are being continued, to which end light dispersion (photo-electric), light refraction and surface tension methods are to be utilized.

[3] Kroepelin, *Kolloid Z.*, **47**, 294 (1929); Kirchhof, *Ibid.*, **15**, 31 (1914).

[4] Represented graphically, S is equal to the surface which is bounded by the curve of the viscosity as a function of the pressure, and by the straight line which runs parallel to the abscissa, and which cuts the ordinate at point η_∞ (η of the solution at the critical pressure, according to Kirchhof).

[5] Bary, *Rev. gén. caoutchouc*, **9**, No. 78, 5 (1932); RUBBER CHEM. AND TECH., **5**, 123 (1932).

[6] If copper is present in the rubber solution, a flocculent precipitate of rubber is formed after a long time. Under the microscope this flocculent mass appears in the form of a screen, the surface of which is covered with the copper salt. The nature of this flocculent precipitate, as well as its formation, cannot be explained at this time. Naturally the precipitate cannot be regarded as originating in the oxidation of the rubber, because when the same experiment is carried out in an atmosphere free of oxygen, the same phenomenon is observed. Conversely, when a rubber solution undergoes actual oxidation in the absence of copper salts, there is no visible formation of a flocculent substance. That the latter represents a modified rubber product is proved by the fact that when a solution of rubber, purified by the method of Pummerer, is exposed to the action of copper salts, a flocculent clot-like precipitate is obtained. We intend to occupy ourselves with the explanation of this phenomenon.

[7] In this is evident a further confirmation of the assumption that the flocculent precipitate of rubber does not in any sense represent an oxidation product of the rubber, for in such a case there would necessarily be a still larger precipitate by the action of ultra-violet light in the presence of benzoyl peroxide.

[8] The determination of the light dispersion was carried according to the photoelectric method of Andreew, *Kolloid Z.*, **43**, 14 (1927).

[9] Experiments with rubber purified by the method of Pummerer gave the same results.

[10] The rubber for the thermochemical experiments was prepared by evaporation of a latex solution to which the copper salt had been added. A control test was carried out on a latex film free of copper.

[11] The experiments on the action of copper salts added during milling are being continued.

[Translated for Rubber Chemistry and Technology, from Bulletin de la Société Chimique de France, Vol. 1 (5th Series), No. 1, pages 83–85, January, 1934.]

The Degradation of Rubber Solutions

P. Bary and E. Fleurent

[In the Bulletin de la Société Chimique de France, Vol. 1 (5th Series), No. 1, pages 69–85, January, 1934, the authors have assembled in connected form and with but few modifications the several previous papers dealing with the same subject. These earlier papers have been published in RUBBER CHEMISTRY AND TECHNOLOGY.[1] However, there is in the new paper an additional section, entitled "Chemical Changes Accompanying Degradation," an English version of which is given below.]

Chemical Changes Which Accompany Degradation

From the beginning of our experiments[1] we have called attention to the fact that the character of the degradation varies not only with the prevailing temperature but also with the solvent used. In particular, if one compares the solutions obtained by the degradation of a given rubber (pale crepe) at a concentration of 0.02 in aromatic hydrocarbons, it is found that the color of the solution changes in the following way:

In benzene at 80° the degraded solution remains colorless.
In toluene at 93° the degraded solution becomes golden yellow.
In xylene at 138–140° the degraded solution becomes dark brown.
In cumene at 150–155° the degraded solution becomes brown-yellow.

The temperature takes part in these changes through a pyrogenic action which in the case of xylene, can easily be detected by the odor, but this is not the only cause since cumene, used like xylene at the boiling temperature, gives a much lighter solution than would have been expected, and there is no pyrogenation or only a very slight one.

Moreover, it is observed that when the degradation has reached a sufficiently high point, coagulation of rubber by the addition of alcohol or of acetone becomes impossible, and sometimes a very stable emulsion is formed, but the part emulsified does not represent anywhere nearly the total quantity of rubber, since the latter has been converted to a great extent into a form soluble in acetone. If the solution is evaporated by a method which makes possible a determination of the rubber it contained when it was not degraded, the quantity found after evaporation is very much less than that which should be present, and furthermore the product obtained is in a pasty state, almost liquid and gluey, as rubber would be if it had turned to a fatty condition.

On the other hand, when the degradation is sufficiently advanced, there is formed after standing an insoluble precipitate at the bottom of the vessel, which is not very great, and which is not formed in a solution which has not been degraded, or only when it is very dilute and after a sufficiently long time. However, these latter conditions are the very ones which correspond to degradation itself at laboratory temperature. In both these cases the precipitate consists of a whitish or gray substance which can be separated or washed with acetone and then evaporated. In weight it represents 2 to 2.5 per cent of the quantity of rubber in the solution. A nitrogen determination by the Kjeldahl method gives, in its general order of magnitude, the same proportion which is found in the proteins of rubber, *i. e.*,

approximately 12 to 13 per cent of nitrogen. It may be concluded from this that the degradation has resulted in a separation of the proteins from the rubber and has made it possible to precipitate them.

These results apply to rubber degraded in the presence of air. When the work was carried out in a vacuum, the same precipitate of protein was obtained, but it was then much darker in color, in fact almost black, at least when the degradation took place at 92° C.

It appears therefore as if the separation of the proteins from the dissolved rubber is a result of the degradation of the latter, *i. e.*, the proteins are liberated at the same time that the structure of the solution disappears. Although these results do not prove that the proteins form part of the substance of which the structure of the solution is composed, nevertheless it may be concluded from their separation simultaneously with the loss of the structure of the solution that these two phenomena have one and the same cause.

In numerous investigations, some of which are quite old, various authors assumed that there was a combination of the solvent with the rubber; this is the conclusion reached in the works of Caspari[2] and of Kirchhof.[3] However, numerous substances added to rubber solutions are capable of changing the viscosity of these solutions and, as a result, are capable of influencing the state of dispersion of the substance in solution. In addition to oxygen, which has already been discussed here and the influence of which is considerable, Fol[4] has proved the important part played by resins which are normally present in natural rubber.

This same fact has been confirmed by Stevens.[5] In a more recent work, Eggink[6] has shown that the viscosity of benzene solutions of rubber is reduced by the addition of even very small quantities of different acids such as benzoic, acetic, hydrochloric, and sulfurous, whereas the addition of ammonia produces the opposite effect.

We think that to the fortuitous presence of foreign substances and to their effect, even in very slight quantities, on the viscosity of solutions must be attributed the relatively large number of our experiments in which the results have shown variations which were sometimes 20 to 50 times greater than the material errors possible in measurements. The foreign substances may come from the solvent and from prolonged contact with the walls of the receptacles containing the solutions, but they may also be introduced with the rubber itself, of which it is impossible to say that two samples taken from a single piece have absolutely identical compositions.

It therefore seems probable that rubber solutions, like the natural substance itself from which they are prepared, are composed of two types of dispersed molecules; the first are highly polymerized and form in the mass a sort of irregular network which makes up the structure, while the second type is less highly polymerized and its total mass has much more influence. Small quantities of substances reacting on the structural polymers would be sufficient then to modify considerably the apparent viscosity of the total volume of the solution.

References

[1] Bary and Fleurent, *Rev. gén. caoutchouc*, **8**, No. 73, 12 (1931); **9**, No. 78, 3 (1932); *Compt. rend.* **193**, 852 (1932); **195**, 665 (1932); **196**, 1796 (1933); RUBBER CHEM. AND TECH., **4**, 505 (1931); **5**, 121, 123 (1932); **6**, 111, 376 (1933).

[2] Caspari, *J. Chem. Soc.*, **105**, 2139 (1914).

[3] Kirchhof, *Kolloid. Z.*, **15**, 30 (1914).

[4] Fol, *Eighth Congress of Applied Chemistry*, **9**, 71 (1912).

[5] Stevens, *India Rubber J.*, **46**, 345 (1913).

[6] Eggink, *Rev. trav. chim. Pays-Bas*, **42**, 317 (1923).

[Translated for Rubber Chemistry and Technology from Revue Générale du Caoutchouc, Vol. 11, No. 102, pages 3–4, June, 1934.]

The Viscosity of Latex

Paul Bary

Latex, like most emulsions, has complex properties which make its use at times difficult because of somewhat unexpected phenomena which take place within the mass.

The properties of this material, whose usage is spreading more and more, are therefore of practical interest, and this has led us to publish the results of some investigations on the viscosity of latex and the conclusions which seemed to be justified by these experiments.

The viscosity of a normal latex containing 38 per cent of rubber is about 4.6 times as great as that of water. This is true of a latex containing a little ammonia, such as the grades which can be purchased in France. The same latex, concentrated to 60 per cent, or "Jatex," is almost 42 times as viscous as water, *i. e.*, more than 10 times as viscous as 38 per cent latex.

Moreover, if latex of different concentrations is prepared by dilution of 60 per cent latex, it is found that the viscosities are those given in the accompanying table, expressed as relative viscosities, based on the viscosity of water.

The curves in Fig. 1 show that the values of $\log \eta$, which would have to be on a straight line if the formula of Arrhenius were applicable, give a line which has a sharp bend, showing that the viscosity increases more rapidly than the exponential function of the concentration of the latex.

It may at first glance seem surprising that the viscosity increases so rapidly with the increase in concentration. However, it is easily understood that the reason for this is the slight distance between the granules when the concentration approaches 60 per cent.

If it is assumed, in order to simplify things, that rubber has the same density as latex, which is not very far from the truth, and that the granules are all spherical and of a diameter of 1 μ, then one can easily calculate the volume of each granule as 0.525×10^{-12} cc. The number of granules in a cubic centimeter of latex is therefore:

At a concentration of 38%	74×10^{10} per cc.
At a concentration of 60%	114×10^{10} per cc.

Now the most concentrated emulsion which one can expect corresponds to the state where all the granules come into contact without being deformed, or at least to the point beyond which the viscosity is such that the emulsion no longer flows like a liquid, but forms a more or less plastic paste. This concentration is then 74 per cent, as may be easily calculated. Greater concentrations can of course be considered by assuming a deformation of the spherical granules, which would be transformed little by little into rhomboidal dodecahedrons, which would be obtained at a concentration of 100 per cent if the rubber had been previously coagulated.

The calculated concentration of 74 per cent is independent of the size of the granules of the rubber, provided that all the granules are spherical and are all of the same diameter.

Accordingly this is very far from the actual case, since neither one nor the other of the conditions is fulfilled in natural latex. Granules which are not spherical are

able to occupy more room than the others, but on the other hand the spaces left between the large granules may be occupied by others very much smaller. It is easily conceivable then that concentrated emulsions may be obtained containing a maximum which is greater or less (varying with the condition) than the calculated value of 74 per cent.

Nevertheless if at a concentration of 74 per cent the granules are in contact with one another, it is possible to determine to what extent the diameter of 1 μ of each granule must be reduced for the concentration to become 60 per cent. Evidently

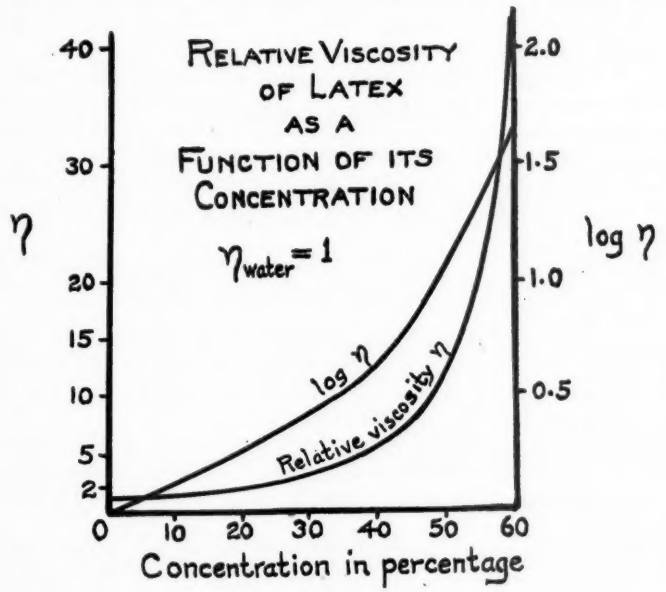

Figure 1

it would be sufficient if the respective volumes are in the relation of 60 to 74. Accordingly:

	Concentration	Rate of Flow in Seconds	Relative Viscosity η	Log μ
Pure Water	0.0	52	1	0.0
Latex	0.14	71	1.36	0.133
Latex	0.24	107.3	2.06	0.314
Latex	0.38	239	4.6	0.663
Latex	0.48	504	9.9	0.995
Latex	0.60	2018	42	1.623

$$\frac{D_1^3}{D_2^3} = \frac{60}{74} \text{ or } D_1^3 = \frac{60}{74} D_2^3 = 0.81 \quad \text{and } D_1 = 0.93\,\mu$$

Since the distance from center to center of the granules is in each case 1 μ, the interval left between them, which is zero for the 74 per cent latex is equal to 0.070 μ for 60 per cent latex, whose granules are supposed to have a diameter of 0.93 μ.

The small dimension of free passages between the granules explains why albuminous substances already present in the natural product are able to rapidly change a liquid mass into a thick paste, since these substances have two modes of action which act concurrently to bring about this result:

(1) The increase in the viscosity of the serum by the addition of hydrophilic substances, *i. e.*, substances which swell and can even be dispersed in water.

(2) The phenomenon of adsorption produced at the surface of the granules increases their exterior diameter and reduces the already slight distance which separates the granules one from another.

Moreover, each of these modes of thickening probably acts in a different way. The first method brings about a true and persistent thickening upon agitation, whereas the second method is manifest in more or less rigid bonds created between the granules at rest, but these bonds are easily broken by a sufficiently vigorous agitation; furthermore they form again when the substance is again let stand.

In any case it is remarkable that very small quantities of hydrophilic substances are capable of imparting a high viscosity to latex, sometimes to the extent of forming semi-solid creams, which are of interest in the preparation of latex compounds containing fillers to be used in the rubber obtained subsequently by coagulation.

Experiments show in fact that if 3 per cent of casein is added to latex containing 60 per cent of dry substances, *i. e.*, 5 per cent of casein based on the rubber in the latex, there is obtained a fairly stiff paste when the experiment is carried out in the following way.

Powdered casein is treated with 12 to 15 times its weight of water; it is allowed to swell to a maximum and then is added to the latex, with agitation of the whole to obtain good dispersion.

If it is intended to add to the latex a mixture of powders such as sulfur, zinc oxide, accelerator, etc., and if it is necessary to grind and to mix these different substances together, it is important not to add to the mixture the casein used for thickening before grinding the powders in the water.

As a matter of fact, prolonged grinding in water of the casein, as is the case with gelatin or with albumin, results in a degradation of these substances, solutions of which upon grinding diminish in viscosity, as it is well known that they are changed by heat.

The interest in making latex appreciably thicker makes this fact of some importance in a number of products if it is desirable not to add to the rubber too large proportions of casein, which might detract from the qualities of the finished products.

The addition of casein during the grinding of the powders by the usual mechanical means is of interest, however, in that it facilitates the dispersion of insoluble substances, but the casein thus added to latex with the powders plays very little part in increasing the viscosity of the latex. It is therefore necessary in order to obtain the desired thickening to add later a fresh quantity of casein that is swollen to a maximum and has not been degraded mechanically or by heat.

[Translated for Rubber Chemistry and Technology from Kautschuk, Vol. 10, No. 6, 82–83, June, 1934.]

The Formation of Sulfur from Hydrogen Sulfide and Sulfur Dioxide

A Contribution to the Vulcanization Process of Peachey

Lothar Hock and Hans Schmidt

GIESSEN AND BERLIN-KARLSHORST

In the reduction of sulfur dioxide by hydrogen sulfide, the course of the reaction depends wholly upon whether water is present or the gases are dry. With water present, there is a ready separation of sulfur, even at room temperature, according to the general reaction: $SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$, though accompanied by more complicated reactions involving the formation of polythionic acids.[1]

On the contrary at room temperature the dried gases do not react, and only at elevated temperatures do they give rise to sulfur and water vapor, in which case because the reaction is exothermic the equilibrium is displaced more and more toward the original sulfur dioxide and hydrogen sulfide. Conversely then, the formation of free sulfur is favored by lowering the temperature.

The heat of activation of the reaction is however so great, even at room temperature, that the rate of the reaction is imperceptibly small, and accordingly no reaction is observable.

In the presence of rubber, on the other hand, conditions are extremely favorable for activation, because the rubber hydrocarbon plays the part of an acceptor of the liberated sulfur and is vulcanized by it, as Peachey and Skipsey[2] were able to show in their well-known work.

The question then arises whether, in this form of vulcanization, the water which is already present or which is formed plays a decisive role in starting and continuing the reaction (in which case the formation of polythionic acids might also play a part), or whether the essential reaction takes place between the two gases in the dry state, in which case the reaction progresses in a much more unrestrained way than in the absence of substances which activate the reaction.

In view of this, two series of experiments were planned with the object of obtaining a better insight into the reaction. In one series the rate of the reaction with both gases in the dry state was studied by some trial measurements only; in the other series the part played by moisture in vulcanization by the Peachey process and in the vulcanization of rubber swollen in benzene was investigated.

1. The Reaction of Sulfur Dioxide and Hydrogen Sulfide between the Completely Pure and Dry Gases

Although at room temperature the dry gases can stand indefinitely long together without any change,[3] according to the present experiments at higher temperatures, *e. g.*, after about one-half hour at only a little above 250° C., there is a slight deposition of sulfur on the walls of the receptacle containing a mixture of the pure, dry gases. The progress of the reaction can be followed by the decrease in the gas pressure, since it is accompanied by a diminution in the number of molecules.

Accordingly the quantities of gases (in the ratio of 1 molecule of sulfur dioxide to 2 molecules of hydrogen sulfide) in the experiments were at a low enough pressure so that at the particular temperatures chosen the water and sulfur liberated were in the gaseous state, and there was no condensation. The gases were completely purified,[4] thoroughly dried and stored in separate large glass flasks, from which they were led through ground-glass connections and fused glass conduits into the reaction vessels which had previously been carefully evacuated. The volumes thus drawn off were measured by a Hempel burette sealed with mercury.

The preliminary experiments, in which the progress of the reaction was followed, were carried out at 330° C., whereby it was proved that there was no increase in the rate of the reaction when the reaction vessel was filled with glass wool. This indicated that a homogeneous gas reaction is involved, which was not what was to be expected on first consideration. The reaction in the presence of rubber, which is described later, will probably have to be regarded not as a simple wall reaction, but as a reaction which is induced even at room temperature by the specific chemical nature of the rubber.

A preliminary measurement of the rate of the reaction at 308° C. was carried out by filling a quartz pear-shaped flask of 50-cc. capacity, to which a Bodenstein quartz spiral manometer[5] was fused, with a stoichiometric mixture of the two gases at an initial pressure of 134.4 mm. of mercury (89.6 mm. of H_2S and 44.8 mm. of SO_2) measured at 21° C., and then heating the flask in an electric oven at 308° C. for 4 hours. The initial pressure of the gaseous mixture at 308° C., calculated from this, is approximately $(581/294) \times 134.4 = 265$ mm. In the interval of time between 0 and 275 minutes after the beginning of the reaction, there was observed a drop, at first rapid and then slower, in the total pressure from 265 to 220.2 mm. of mercury, *i. e.*, the times and pressures were as follow: 35, 232.6; 50, 228.0; 65, 226.1; 155, 221.3; 215, 220.6.

2. The Reaction between Hydrogen Sulfide and Sulfur Dioxide in the Presence of Rubber (Vulcanization by the Peachey Method)[6]

In addition to the foregoing investigation, the cause of the reaction between the two gases in the Peachey process, *i. e.*, the cold vulcanization of rubber by means of hydrogen sulfide and sulfur dioxide, had to be established in a purely qualitative way. The question was whether the reaction is dependent upon moisture in the gases or in the rubber, or whether the rubber itself can initiate the reaction. The experiments to obtain an answer to this question were carried out both with solid rubber and with swollen rubber, for which purpose the apparatus described below was used (see illustration).

After the substance, the influence of which on the reaction was to be studied (sulfur as well as rubber was tested), had been placed in the reaction vessel *a*, the latter was fused onto the stopcocks 1 and 2. With stopcocks 1 and 2 open and 3, 4, 5, and 6 closed, the system was evacuated through *e*, with the special object of drying thoroughly the rubber inside. After closing stopcock 1, a slow current of air, which had been previously dried through calcium chloride and phosphorous pentoxide, was passed in through *e*. In the case where benzene was to be introduced into *a*, stopcocks 2 and 3 were first opened, then stopcock 4 was opened cautiously so that the benzene was sucked into the evacuated reaction vessel. The benzene, which was the purest thiophene-free grade, had been let stand for 5 months over sodium. After stopcock 4 was closed, stopcocks 6 and 7 were slowly opened, and finally stopcock 1 was also opened. The reaction vessel *a* was then open through the drying tubes to the outside air. Dry sulfur dioxide and

hydrogen sulfide could then be led into reaction vessel *a* to the desired extent. The sulfur dioxide was generated from sodium bisulfite and sulfuric acid, the hydrogen sulfide from calcium sulfide and hydrochloric acid. The acid vapors were absorbed in sodium carbonate solution. Both gases were dried in calcium chloride and phosphorous pentoxide tubes.

As a beginning, an experiment described by Klein[7] was reproduced in this apparatus. Vessel *a* was filled only with benzene, and the latter was saturated with hydrogen sulfide and sulfur dioxide. In agreement with Klein, there was no reaction even after 4 hours.

In view of this, in the next experiment a glass rod covered with a thin film of pure Para rubber was placed in vessel *a*, was dried by evacuation and warming for one-half hour at about 60° C., after which it was immersed in benzene, and dry hydrogen sulfide and sulfur dioxide were passed through.

Neither in the benzene itself nor on any part of the glass walls of the vessel was there any reaction even after 16 hours, whereas within one-half hour after the gas current was started, the previously clear swollen rubber had become opaque, *i. e.*, vulcanized, and sulfur had deposited on it. It is worthy of note that the reaction was confined to the surface of the rubber and did not spread into the benzene. It was natural to expect that the water liberated in the reaction would diffuse into the benzene and induce a continuance of the reaction in the benzene. A test was therefore carried out to determine whether perhaps there would be a reaction in benzene containing more water. Benzene was agitated for one-half hour with an excess of water, and after standing was removed from the underlying layer of water. However, even after hydrogen sulfide and sulfur dioxide had been led for five hours through this benzene saturated with water, there was no perceptible change.

A further experiment was carried out to determine whether sulfur catalyzes the reaction between the two gases. Sulfur recrystallized from carbon disulfide was finely pulverized, was extracted with water to remove any oxidation product, and was then dried in vessel *a* by evacuating and warming to about 90° C. Hydrogen sulfide and sulfur dioxide were then led in in the usual way, but here too there was no reaction, even after 4 hours.

Finally dry hydrogen sulfide and sulfur dioxide gases were made to act upon pure Para rubber in the absence of benzene. To this end, a few drops of a solution of Para rubber in benzene were placed in vessel *a*, and the solvent and water were then removed by evacuation and warming at about 60° C. for 2 hours. About 20 minutes after introduction of the dry gaseous mixture the rubber became turbid. The reaction started in the rubber and then spread to the glass walls, evidently through the agency of the water film which was formed.

Summary

As a result of the experiments, it may be said that in the Peachey process of vulcanization, dry rubber itself is capable of bringing about the reaction between hydrogen sulfide and sulfur dioxide, under which conditions it seizes the sulfur which is liberated. Once started, the reaction spreads wherever there is a sufficiently high concentration of the water which is already liberated in the reaction. It may be, as happens in the presence of water, that the two gases react with one another with formation of polythionic acids and sulfur, but where rubber is present as an acceptor of the liberated sulfur, there may be a chemical catalytic effect on the reaction between hydrogen sulfide and sulfur dioxide, which begins in the complete absence of water.

Comments by St. Reiner

A. E. G. Kabelwerk, Oberspree

In view of the results published by Hock and Schmidt in the foregoing paper, it seems opportune to describe some experiments in the same field which were carried out a long time ago.

The question arose whether it was possible to continue the gas vulcanization by the Peachey process to the state of hard rubber, and whether the sulfur formed from the gases diffuses through relatively thick layers of rubber even after a crusting of the surface of the rubber has taken place. In order to study this, a strip of sheet rubber about 10 mm. wide, attached to a glass plate, was suspended in a large test tube. Two glass tubes carrying hydrogen sulfide and sulfur dioxide projected into the test tube through a cork stopper sealed with paraffin, and another tube served as an outlet for the gaseous mixture. The whole system was immersed in an oil bath; one thermometer showed the temperature of the oil bath and another the temperature of the contents of the test tube. The sulfur dioxide was prepared from bisulfite and sulfuric acid, and the hydrogen sulfide from iron sulfide and hydrochloric acid. They were dried over calcium chloride.

Experiment 1.—Both gases were passed over strips of sheet rubber about 3 mm. thick for 5 hours at 135° C. At the end of this time, a slight vulcanization was evident. The strips had a certain elongation and strength but only a slight turbidity.

Experiment 2.—A further study was carried out to determine whether accelerator "C.T." incorporated in the rubber accelerated the gas vulcanization. To this end 1 per cent of "C.T." was added to the sheet rubber, the latter was then sheeted out into strips 3 mm. thick, fastened onto a glass plate, and placed in the test tube. The gas reaction was carried out at 135° C. At the end of three and one-half hours the strip was strongly vulcanized, and the outside had a brittle surface. The experiment was continued for 48 hours. At the end of this length of time the surface of the strip had become black and shiny. When the surface was broken, the formation of hard rubber and the diffusion of sulfur for about 2 mm. was plainly evident. Approximately 1 mm. of the interior remained brown and tacky. An analysis of the sulfur content of a sample removed from the surface of the vulcanized strip showed approximately 28 per cent of sulfur.

The results of Hock and Schmidt, which show that even dry rubber brings about a reaction between hydrogen sulfide and sulfur dioxide and then seizes the liberated sulfur, confirm the experiments described above. The reaction which is set going in this way can be continued to the stage where hard rubber is formed. This reaction is accelerated by the presence of an organic accelerator such as "C.T."

[From *Kautschuk*, Vol. 10, No. 8, page 128, August, 1934.]

References

[1] Ephraim, *Anorganische Chemie*, 4th Ed., page 468.
[2] *J. Soc. Chem. Ind.*, **40**, 5 (1921).
[3] Schmidt, *Chem.-Ztg.*, **11**, 50 (1868); Heinze, *J. prakt. Chem.*, [2], **99**, 109 (1919).
[4] Moser, *Reindarstellung von Gasen.*
[5] *Z. phys. Chem.*, **69**, 26 (1909).
[6] Peachey, *J. Soc. Chem. Ind.*, **40**, 5 (1921).
[7] Klein, *J. phys. Chem.*, **15**, 1 (1911).

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Some Observations on Accelerator Practice and Modern Compounding

R. C. Davies

In the last twenty-five years a number of complex organic compounds have been developed and patented for the purpose of accelerating the vulcanization of rubber. Really serious bulk usage throughout the trade, however, did not commence until after the war. Research in this field raced ahead of manufacturing progress and brought out accelerators which were so active that they were almost unusable.

There are now accelerators which are more than sufficient for the needs of the moment. They cover all ranges of conditions, such as slow, medium slow, semi-fast, semi-ultra, ultra, and super-ultra accelerators. In addition there are modifications for delayed action, quick start, flat peak, high tensile, and superflexing; also accelerators which will cure without heat and others which will cure without added sulfur.

In view of the publicity indulged in by the vendors, one might almost feel compelled to change one's accelerators every week. Rationalization is as necessary in the use of accelerators as in the use of fillers.

In the wise use of accelerators it is necessary to make a careful selection of only a few which function best in the temperature and process range of any particular manufactures.

An extensive knowledge of the properties and behavior of each accelerator as applied to any particular process is necessary before skillful manipulation can be indulged in with advantage.

There is as yet no universal accelerator. Generally speaking the faster accelerators have a wider field of application in the general trade than in the tire trade.

Processing difficulties are the main stumbling blocks in the mass usage of ultra-accelerators. The rapid development of anti-scorching ingredients as a means of overcoming this is virtually the line of least resistance, and serves to mask the lack of complete appreciation of the factors governing the safe use of ultra-accelerators. A specific example will serve to explain how these factors can be estimated.

In the manufacture of modern rubber footwear, comprising everything from a bathing shoe to a heavy industrial thigh boot, there is a range of articles as widely different in size, shape, and thickness as a cycle tire and a giant pneumatic, or a water-bottle and a heavy belting. As a complication there is the heavy thigh boot with a combined sole thickness of about one inch, with the top extension gaging about $^1/_{16}$ inch. This must be cured as a unit without over- or undercure of any part.

It is economically advantageous if a thin article like an all-rubber bathing shoe can be cured in the same heat. Such conditions can be easily obtained with a wise choice of accelerator combinations. The choice depends upon the following main factors: (1) the average mixing roll temperature; (2) the average calender temperature; (3) the average resting time of stock between processes or during week-ends and holidays; (4) the rate of transference of heat through a given thickness of

canvas or rubber; (5) the time required to raise the internal metal (lasts and heater-cars) to curing temperature and the suggested curing temperature, and (6) the average stocking time and average expected life of the articles.

Bearing upon the above points are the following subsidiary corollaries. (1*a* and 2*a*) It is cheaper to make accelerators conform to the existing mill and calender plant than to modify the plant or increase the usage of cooling water. (3*a*) It is cheaper to make stocks non-scorching than to install quenching devices after mixing. It is cheaper to be able to leave processed stock during a holiday for convenient restart than to shut down and restart, by stages, to avoid curing up. (4*a* and 5*a*) Lasts give a quicker turnover if large and small, and thick and thin articles can be bulked in the same heat. Heaters and heater-cars are used to capacity in spite of a varied ticket. It is more economical and gives better products to cure at low temperatures than high. Short cures are economical. (6*a*) The resistance to aging must exceed the total life of the article by a wide margin.

A selection of three accelerators will cover all the conditions, but in order to avoid modifying the process for the sake of one or two exceptional articles requiring special treatment, an addition of one or two more is an advantage.

These should be of the following type: (*A*). An ultra type with a quick vulcanizing action at low temperatures, such as the zinc salt of dithiocarbamic acid. (*B*). A semi-ultra which can modify *A*, such as tetramethylthiuram disulfide (*C*). A low-price fast-medium, inactive at low temperatures and flat-curing at high temperatures, such as mercaptobenzothiazole. (*D*). A low-priced slow-medium, inactive at low temperatures, capable of giving fast eutectic combinations with *C* at a low cost, or of modifying *A* or *B* at low temperatures, such as diphenylguanidine. (*E*). A low-priced slow-medium, inactive at low temperatures, and capable of forming double, triple, or quadruple combinations with *D*, *C*, and *B*, such as hexamethylenetetramine.

The number of permutations possible with five accelerators, together with the variable proportions possible in double, triple, and quadruple combinations, runs into thousands. Any peculiar combination of circumstances, processes and variety of article can be adequately dealt with. No single accelerator can be called upon to meet such varied conditions alone.

With low temperature curing conditions of say 240° F. with a maximum curing time of one hour exclusive of the rise, as in general footwear mixings of the accelerated type which have low total sulfur and negligible free sulfur, a fast accelerator combination is necessary.

In order to avoid process troubles and scorching, the local safety factor dependent upon conditions (1), (2), and (3) must be estimated. This can be done in the following manner. Pilot test mixings, containing accelerators of varying degrees of activity and in various combinations, are run through the complete process prior to curing and subjected to all the possible variables of temperature, re-milling, and shut-down stocking.

In order to allow for the use of a percentage of returning cutting waste from all parts of the factory, the stocks are then re-processed a second time. At the end of the test, combined sulfur estimations and plasticity tests are made.

As the plasticity is a variable which can be readily modified to suit conditions, the combined sulfur figures are of most importance, being a direct estimation of the degree of scorching.

It will be found that certain fast accelerated mixings return a high combined sulfur of the order of 0.8 per cent out of a possible coefficient of 2.5 per cent. These mixings will be found to be already scorched and will not re-mill. Others with

slower accelerators, or safer combinations, will return a figure of say 0.1 per cent after the first processing, and perhaps 0.2 per cent after a second processing. These will be found to be capable of re-milling almost indefinitely, and will withstand long storage in the uncured state.

It now remains to fix a limit as a safety factor. Let it be assumed that it is 0.5

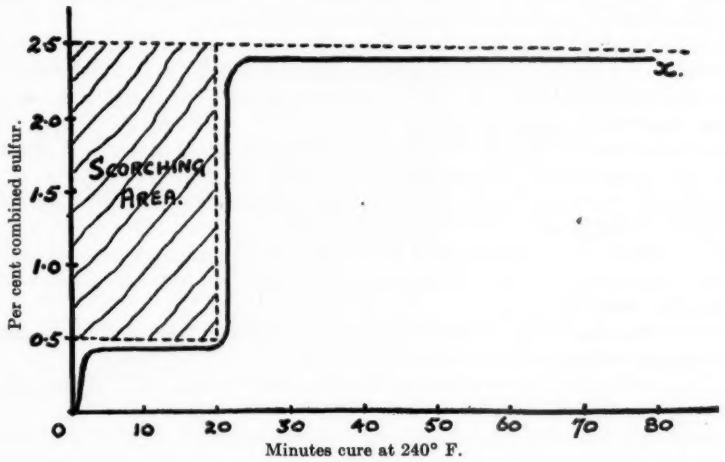

Figure 1

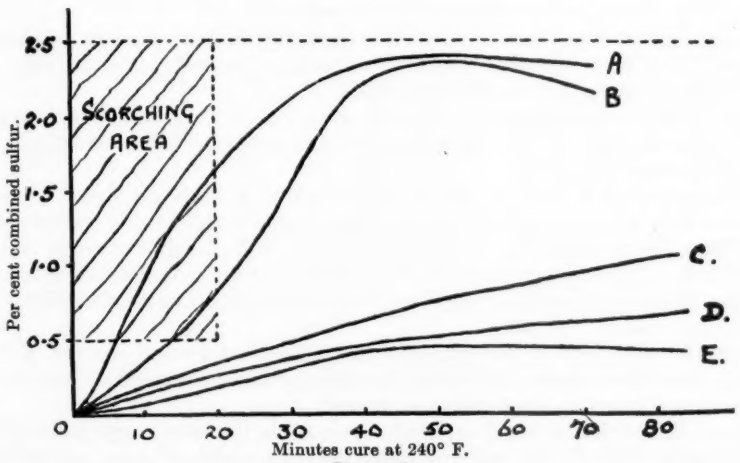

Figure 2

per cent combined sulfur. This means that any mixing returning a combined sulfur below this, after complete processing, will be safe for these particular conditions.

Now comes the question of curing. Let it be assumed that the maximum time required to raise the temperature of the lasts, heater-cars, and metal parts to a uniform curing temperature of 240° F. is one hour.

For the purposes of laboratory experimental cures, where the conditions of the rise in a factory heater cannot easily be repeated, the time of one hour rise can be

made equivalent to a fixed temperature. It may be assumed that for practical purposes, twenty minutes at 240° F. is equivalent to sixty minutes rise to 240° F. Therefore, in order to avoid wide discrepancies in the rate of curing because of different sized articles having a different heat absorption, it is advisable to limit the amount of vulcanization that takes place before the articles reach a uniform temperature. This limitation of accelerator activity in the early part of the cure can be correlated with the similar limitation during processing.

Let it be specified then that no mixing shall attain a coefficient of 0.5 per cent sulfur out of a possible total of 2.5 per cent during an equivalent vulcanizing time of twenty minutes at 240° F. As this temperature is normally well above the average processing temperatures in conditions (1), (2), and (3), such a factor should render the compounds virtually fool-proof in mixing, processing, and curing.

This can be expressed graphically in the following manner (see Fig. 1). The curve in Fig. 1 represents the theoretically ideal vulcanizing curve for the conditions mentioned. Such a curve is of course impossible.

From the figure it is observed that the maximum advantage is taken of combining sufficient sulfur to give initial set-up in the first twenty minutes of the cure without invading the scorching area.

After twenty minutes of delayed action, the maximum "kick-up" of the accelerator is required to take full advantage of the time.

The top portion of the curve should be flat, with a prolonged plateau effect to avoid reversion from overcure.

It is now interesting to see how each of the accelerators *A*, *B*, *C*, *D*, and *E* behave in relation to this curve.

In laboratory tests a mixing of the following composition was used; rubber, 100; sulfur, 2.5; zinc oxide, 2; stearic acid, 1; accelerator 0.5.

The curves in Fig. 2 represent the results with the five specimen accelerators. Curves *A* and *B* are dangerous in that they invade the scorching area, while *C*, *D*, and *E* are too slow at the temperature of 240° F.

The problem of blending two, three, or even four of these accelerators to give a closer approximation to the theoretical becomes more or less mathematical, aided by a little sound reasoning.

With variations of 0.05 per cent of each accelerator, beginning first with double combinations, a few dozen interesting mixings can be made showing material deviations from the curves in Fig. 2. For example, curve *B* is not far removed from the theoretical. It requires the addition of a fraction of a per cent of a slow accelerator, inactive at low temperatures, like *C* or *D* to exert a limiting or delaying action during the first twenty minutes.

With the early part of the cure safe, the addition of a small amount of *A* will tend to bring the intermediate part of the curve nearer the vertical by reason of the fast action of two ultra-accelerators combined.

The small addition of *A* will not render *B* unsafe in the early stages for the following reasons. First *C* or *D* will also delay the early action of *A* as well as *B*, and secondly, in multiple accelerator combinations there is a selective catalytic action in the early stages. It can be proved that, for example, in mixtures of the *A* and *B* types, though *A* is the faster accelerator ultimately, *B* goes into action first in a mixture by virtue of some properites it may possess, such as lower melting point or easier solubility in the rubber.

Hence a combination of *A* and *B* will not necessarily cut the scorching area, though each does so individually.

The lengthening of the plateau effect may be obtained by varying the amounts of

C, *D*, or *E* which, though limiting the fast accelerator in the early stages, is not fugitive, and comes into action at the end of the cure.

Some of these accelerators *C*, *D*, and *E* are also mild anti-oxidants and do not suffer from heat degradation with over-cure so readily as the *A* and *B* types.

There is yet another type of combination which is effective and has the advantage of cheapness. There are many combinations of low-priced slow accelerators like *C*

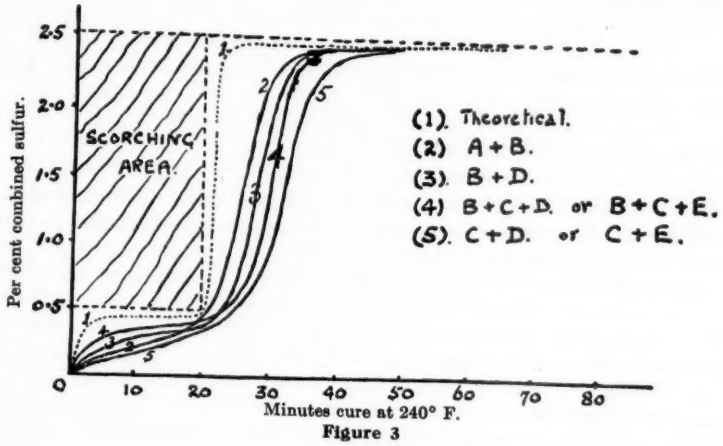

Figure 3

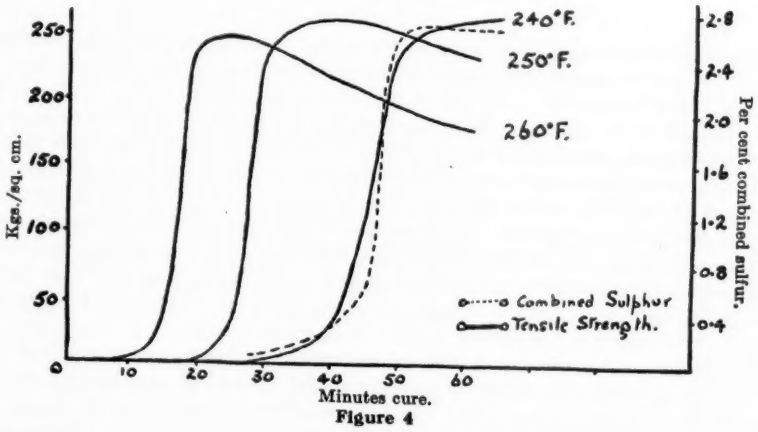

Figure 4

D, or *E* which have what may be called eutectic spots. In these particular proportions they behave more like *A* or *B*, but at a lower cost.

A few examples of how nearly the theoretical curve can be approached using various dissimilar combinations may be seen in Fig. 3.

A few well-chosen combinations like this will be as easy to operate as any single accelerator.

It is advisable, when making calculations for multiple accelerator combinations, to have some unit which expresses the worth of the combination. This unit should be representative of price, speed, and quantity required for a given result.

The ultimate choice of vulcanizing temperature is dependent upon local factory conditions and the time cycle of operations required. Slight changes in the vulcanizing temperature do not materially effect the shape of the vulcanizing curve, once the fundamentals have been fixed. It is, however, difficult to correlate a 240° F. air pressure cure with a 50 lb. steam pressure press cure for rapid laboratory testing, as such a temperature change is outside the range of adaptability for such accelerator combinations.

Nevertheless, although vulcanization curves at such widely differing temperatures as 240° F. and 297.5° F. (50 lb. steam) have little relationship in the early stages, the physical properties at the optimum can be correlated by a factor with sufficient accuracy to enable check tests to be made rapidly for variability control.

Figure 4 shows the physical behavior of a triple accelerator mixing of the *B*, *C*, *E* type at three different temperatures, *viz.*, 240, 250, and 260° F.

For the 240° F. cure, the combined sulfur curve is drawn (see Fig. 4).

Having outlined an organized scheme for the systematic utilization of modern accelerators, it would perhaps be of interest to examine some variables which occur in special conditions, and which are not generally encountered.

In the vulcanization of rubber articles by molding, conditions prevail which tend to mask the instability or lack of homogeneity of the loading materials. The formation of a complete and uniform skin on the surface of the rubber by mold contact has a deterrent action on filler migration which is perhaps beneficial. Nevertheless, many articles are vulcanized without molds, in open steam or dry air. Such goods can be said to have a free or natural surface finish. The examination of the degree of stability of fillers in such conditions gives rise to many interesting speculations.

It is well known for instance, that certain substances which are soluble or partially soluble in rubber, obey the laws of solubility, and tend to come out of solution when saturation is exceeded. Thus, excess sulfur, some accelerators, anti-oxidants, soluble dyestuffs, waxes, and some fatty acid salts bloom. In addition to this it is equally well known that such substances will migrate from one stock to another, as instanced by the vulcanization of stocks containing alternate layers of sulfur stock and accelerator stock, or the migration of colored dyestuffs into white mixings.

If such so-called soluble substances, when in a state of unstable equilibrium, tend to revert to stability, and if the rate of reversion to stability can be influenced by various factors or changes in condition, then might not the same reasoning be applied to so-called insoluble fillers which are to some extent in solid solution.

It is known that other solid solution systems, such as steel or cast iron, tend to change their characteristics with age or under conditions of stress. It is suggested that some rubber compounds will behave in a similar manner.

It is a matter of simple experiment to prove that the migratory blooming of a substance like zinc stearate, which is partially soluble in rubber, can be tremendously accelerated by vacuum treatment. Also it is matter of common occurrence for some migratory substances to carry those which do not normally migrate. For example, a migratory dyestuff will often bring another non-migratory dyestuff to the surface when the two are present in the same mixing, or a wax may carry a dyestuff to the surface with it. This is often a question of preferential solubility. It can also be shown that there is a similar law of preferential solubility operating in respect of insoluble fillers in rubber.

If the normal mixing containing say 20 per cent whiting as loading and 5 per cent iron oxide as coloring agent, is vulcanized in air to avoid the "skin effect," and subjected to outside aging, the filler which is first given up or "exuded" by the rubber will be the iron oxide. It is possible that the nature of the iron oxide itself, acting

as an oxidizing catalyst, accelerates surface decomposition. Nevertheless, though the mixing before exposure contained excess whiting uniformly mixed with iron oxide, washing of the exposed aged surface showed excess iron oxide over whiting. In the same way on external aging of a loaded mixing containing 40 or 50 per cent of whiting, it can be shown that free whiting can be removed from the surface in considerable amounts. It would appear then that few of the ingredients added to rubber are permanently stable, and that the degree of stability can be increased or decreased by various means. The rate of change of the degree of stability may be so slow in some circumstances as to be unnoticeable.

It is possible that for each filler there exists a stable saturation limit for its so-called solid solution in rubber, and this limit is affected by the presence of other fillers.

In view of the effect of this on the ultimate degradation of a compounded rubber due to aging or breakdown under mechanical stress apart from fundamental degradation of the rubber itself it would seem advisable to pay some attention to these factors when compiling a compound in addition to the more usual properties of tensile strength, state of cure, and direct loss of physical strength from aging.

It is also an additional argument in support of the rational simplification of any compound, in order to minimize the variables as far as possible.

Improvements in the wetting power of fillers materially tends toward greater stability of the matrix, and attention is now being directed to this end with the cheaper fillers. This would also reduce the amount of occluded air which is unfortunately introduced with most fillers and which is a potential source of almost unnoticeable micro-porosity which develops during aging, and is probably the first cause of internal degradation of the rubber and breaking away of the rubber film from the filler particle under stress after aging.

There is still a very large amount of work yet to be done before as much is known as should be known about rubber, and the behavior of all the ingredients which may be added to rubber. It may be that, with increasing knowledge, these well-tried fillers will be rejected and something new adopted. Already considerable work has been done on the introduction into rubber of such bodies as organic plastics, synthetic resins, and cellulose derivatives. Substances such as these have properties more allied to rubber and not so fundamentally foreign to its nature as the majority of well-known fillers. Naturally, many of these substances do not fullfil the expectations of the experimentor in the first essay, but it is not unlikely that, when as much attention has been applied to the particular development of these substances for rubber fillers as has been given to the old fillers, mineral loading will cease to be used.

The author wishes to thank the Dunlop Rubber Co. for permission to publish this paper.

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Studies on the Combined Use of Some Different Organic Accelerators

IV. Diphenylguanidine and Dibenzothiazole Disulfide

Itiro Aoe and Hirosi Yokosima

GOVERNMENT ELECTROTECHNICAL LABORATORY, TOKYO, JAPAN

I. Introduction

In the preceding experiments (*J. Rubber Soc. Japan*, **3**, 71–78, 143–151 (1931); **6**, 173–190 (1933)), binary mixtures of (1) mercaptobenzothiazole and diphenylguanidine, (2) mercaptobenzothiazole and methylene-aniline, (3) tetramethylthiuram monosulfide and diphenylguanidine, and (4) tetramethylthiuram disulfide and diphenylguanidine, were made in order to control the behavior of acceleration and to improve the mechanical properties of the vulcanized products. Tests to obtain data on the softening and melting point curves of binary mixtures and the results obtained by their use showed that the combined use of organic vulcanization accelerators improved the vulcanization process and the mechanical properties of the products. In the case of accelerators (1) and (3), a combination of acid and

TABLE I

SOFTENING AND MELTING POINTS

Mixing Ratio (by Wt.) Percentage Guanidine	Percentage Disulfide	Softening Point (° C.)	Melting Point (° C.)
100	0	149	149.5
99	1	139	147
95	5	124	143
90	10	121	138.5
85	15	121	131.5
80	20	120	128.5
75	25	120	126.5
70	30	120	127.5
65	35	119.5	129.5
60	40	120	133
55	45	120	137
50	50	120	139
45	55	121	141
40	60	120	143
35	65	120	145.5
30	70	121	148
25	75	123	149
20	80	125	150
15	85	128.5	151
10	90	133	153.5
5	95	141	155.5
0	100	180.5	181.5

basic substances to form a molecular compound improved the vulcanization process. Though combination (1) was a superior accelerator, it had the fault of causing scorching. Accordingly, the following experiments were carried out with the idea

TABLE II

COMPOUNDINGS FOR SCORCH TEST (BY WT.)

Pale crepe	100
Zinc oxide	100
Sulfur (acid-free)	3
Accelerator[a]	1

Sample No.	Ratio of Accelerators Guanidine	Disulfide
1	100	0
2	90	10
3	80	20
4	75	25
5	70	30
6	56	44
7	45	55
8	30	70
9	15	85
10	0	100

that the substitution of dibenzothiazole disulfide for mercaptobenzothiazole in combination (1) would give the same vulcanization activity with less danger of scorching.

II. Experimental

1. *Samples.*—Commercial diphenylguanidine was purified by recrystallizing once from hot toluene and three times from hot alcohol; the pure white product

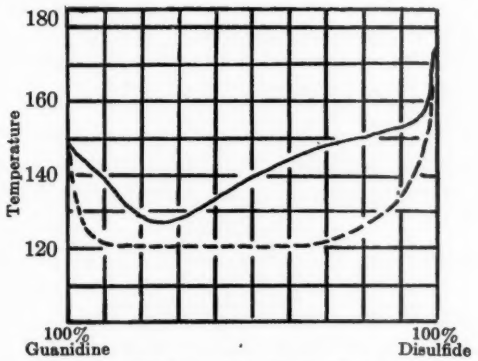


Figure 1—Melting and Softening Point Curve

melted at 149–149.5° C. A commercial dibenzothiazole disulfide was recrystallized several times from hot benzene, digested in and washed with warm alcohol; the pure white product melted at 180.5–181.5° C.

2. *Construction of Eutectic Curve.*—Diphenylguanidine and dibenzothiazole disulfide (hereafter called "guanidine" and "disulfide," respectively) were used in the proportions as indicated in Table I, were mixed well in an agate mortar and pestle, and were placed in a capillary glass tube of 0.5-mm. diameter, to a depth of 5 mm. The softening and melting points of these mixtures were then estimated with the usual apparatus. The results are shown in Table I and in Figure 1.

The estimation of the softening and melting points became difficult as the amount

of disulfide increased. Since the softening and melting points were closest with 75 per cent of guanidine and 25 per cent of disulfide, other combinations of these two ingredients were made around this ratio to find an eutectic point, but the result was negative. Evidently these two ingredients do not form a molecular compound by mixing and fusion. This mixture differs from a mixture of guanidine and mercaptobenzothiazole (cf. the preceding communication) in that it does not form a molecular compound or eutectic mixture, and the softening point is still lower.

3. *Scorching Test.*—The mixtures shown in Table II, were prepared as in the preceding work, and were pressed in sheets of 1-mm. thickness, after standing for 30 minutes cut into discs of 1.6-cm. diameter and heated at 80° and 100° for various

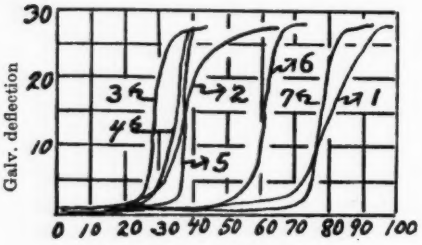


Figure 2A

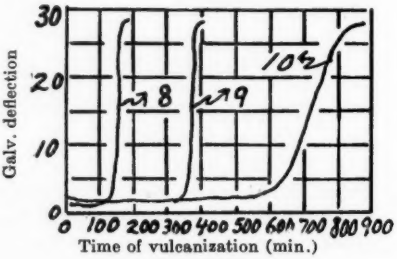


Figure 2B

times, as indicated in Table III. The heated samples were then placed in test-tubes containing 50 cc. of gasoline and shaken up and down at the rate of 300 times per minute for 5 minutes. The amount of zinc oxide dispersed in gasoline in the process of dissolution of rubber was measured by estimation of reciprocal conductivity, using a cuprous oxide photo-cell at 29–32° C.

During the test, the temperature and the distance of the photocell were regulated in such a way that the blank remained at 28 on the galvanometer scale. The results are shown in Tables III and IV and in Figure 2.

In reviewing the data, Samples 1, 2, 3, and 4 heated at 80° C. showed but little change; therefore, these are omitted in the figure. Samples 2 to 5, containing more guanidine, showed more tendency to scorch when heated at 100° C. This effect

TABLE III

RECIPROCAL CONDUCTIVITY FOR HEATING AT 80° C. (DEFLECTION OF GALVANOMETER)

Time of Heating (Min.)	Sample Number									
	1	2	3	4	5	6	7	8	9	10
0	0.7	1.0	0.8	0.7	0.8	0.7	0.7	0.7	1.0	1.0
10	0.9	1.0	0.7	0.7	0.8	0.7	0.7	0.7	0.9	...
20	0.9	0.9	0.7	0.7	0.7	...	...	...	...	...
30	1.0	0.9	0.7	0.7	0.7	0.7	0.7	0.7	...	...
40	1.1	1.1	0.7	0.7	0.8	0.7	...	...	...	...
50	1.0	1.1	0.9	0.7	0.7	...	0.7	0.8	1.0	...
60	1.1	1.1	0.8	0.7	0.7	0.7	...	...	...	...
70	1.0	1.2	0.9	0.7	0.8	0.7	0.8	0.8	...	...
80	1.1	1.3	0.9	0.7	0.8	...	...	...	...	...
90	1.0	1.3	1.0	0.9	0.8	0.8	0.7	0.9	...	...
100	1.2	1.3	1.0	0.9	0.8	0.8	...	0.9	1.0	...
110	1.0	1.8	0.9	1.0	0.8	0.8	0.8	0.9	...	...
120	1.1	2.0	1.0	...	0.9	0.8	...	...	...	...
130	1.1	2.0	1.3	1.2	0.9	0.7	0.7	1.0	...	...
140	0.9	2.1	1.1	1.2	0.9	0.7	...	...	...	...
150	1.2	1.8	1.0	1.1	0.8	0.7	0.8	1.0	1.0	...

was less prominent in Sample 6. Sample 4, containing the accelerators in a ratio to give the closest melting and softening points, showed more scorching.

4. *Vulcanization Experiment.*—The samples were compounded as indicated in Table V, and vulcanized by steam at 30 lb. pressure per square inch. The re-

TABLE IV

RECIPROCAL CONDUCTIVITY FOR HEATING AT 100° C. (DEFLECTION OF GALVANOMETER)

Sample Number									
1		2		3		4		5	
T. H.	G. D.	T. H.	G. D.	T. H.	G. D.	T. H.	G. D.	T. H.	G. D.
0	0.7	0	1.0	0	0.7	0	0.7	0	0.8
10	0.7	10	1.1	5	0.7	5	0.8	10	0.7
20	0.9	20	1.7	10	0.6	10	0.9	15	0.8
30	1.1	30	3.9	15	0.8	15	0.9	20	0.8
40	1.2	40	19.1	20	1.1	20	1.1	25	0.9
50	1.5	50	25.6	25	1.9	25	3.9	30	1.3
60	2.1	60	27.1	30	19.8	30	13.7	35	1.7
70	2.9			40	27.3	35	27.6	40	27.4
80	13.3								
90	23.7								
95	27.3								

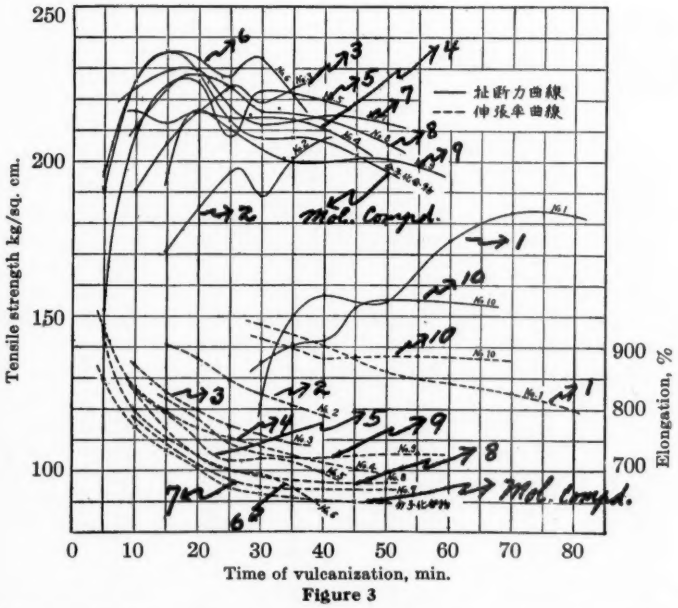


Figure 3

sults of the tensile strength and the maximum percentage elongation measurements with a Schopper apparatus are given in Table VI and in Fig. 3.

The results show clearly that the combined use of accelerators give far better results than their use separately.

The maximum tensile strength of the vulcanized products was the highest in Sample 6, which contained the accelerators in the ratio or 56 per cent of guanidine and 44 per cent of disulfide in their molecular ratio of 2:1. This is the ratio at which they should form a molecular compound, mercaptobenzothiazolediphenylguanidine, when reduced.

TABLE IV (CONTINUED FROM PAGE 651)

Sample Number 6		7		8		9		10	
T. H.	G. D.	T. H.	G. D.	T. H.	G. D.	T. H.	G. D.	T. H.	G. D.
0	0.8	0	0.7	0	0.9	0	1.0	0	2.1
10	0.7	20	0.7	10	0.9	50	1.0	50	1.4
20	0.7	40	0.7	30	0.9	100	1.2	150	1.7
30	0.8	60	0.8	50	0.9	150	1.1	250	1.9
40	0.8	70	1.0	70	0.9	200	1.3	350	1.9
50	1.8	75	4.7	90	1.0	250	1.3	450	1.7
60	8.0	80	19.7	110	1.1	290	1.5	550	1.9
70	27.9	90	19.7	120	1.4	340	1.8	650	5.0
				135	2.0	360	6.3	750	20.2
				140	3.8	380	25.8	850	27.7
				150	11.1				
				160	28.0				

T. H. = Time of heating in minutes.
G. D. = Galvanometer deflection.

TABLE V

COMPOUNDINGS FOR THE VULCANIZATION EXPERIMENTS. (BY WT.)

Pale crepe	100	Sulfur (acid-free)	3
Zinc oxide	5	Accelerator[a]	1

[a] The ratios of accelerators in Samples 1 to 10 are the same as in the scorching tests in Table II.

TABLE VI

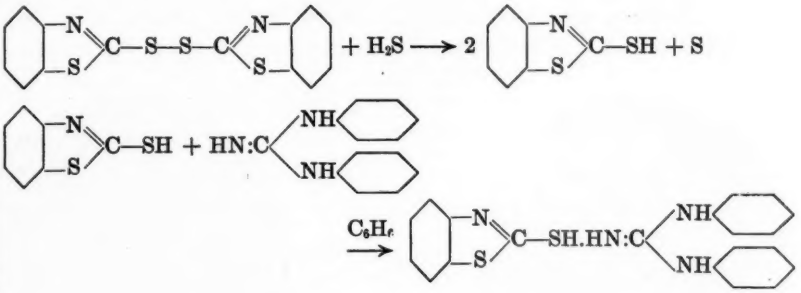
VULCANIZATION TESTS AT 30 LB. PER SQ. IN.

Sample No.	Time of Vulcanization (Min.)	Tensile Strength (Kg. per Sq. Cm.)	Maximum Elongation (Percentage)	Sample No.	Time of Vulcanization (Min.)	Tensile Strength (Kg. per Sq. Cm.)	Maximum Elongation (Percentage)
1	30	121.1	936.3	6	5	196.5	917.0
1	40	156.7	902.6	6	10	226.0	795.5
1	50	154.7	880.2	6	20	233.0	724.5
1	60	174.3	841.3	6	25	227.3	700.4
1	70	183.3	826.3	6	30	233.0	694.3
1	80	182.3	798.4	6	35	221.4	674.8
2	15	171.1	904.3	7	10	223.7	784.6
2	20	185.0	882.3	7	20	229.1	710.4
2	25	196.4	845.7	7	25	217.2	684.6
2	30	188.7	823.3	7	30	212.0	674.8
2	35	201.1	805.0	7	40	214.7	669.4
2	40	207.5	789.8	7	50	212.5	669.8
3	10	190.7	871.5	8	10	211.3	828.5
3	15	206.1	826.6	8	20	228.0	722.6
3	20	216.0	798.7	8	25	224.2	702.2
3	25	224.2	771.3	8	30	216.1	692.0
3	30	219.0	750.8	8	40	213.2	680.2
3	35	224.3	744.5	8	50	205.6	682.1
4	10	216.5	834.8	9	15	196.0	817.2
4	15	212.3	797.3	9	20	216.8	783.2
4	20	216.1	769.7	9	25	210.3	743.8
4	25	214.0	755.3	9	35	199.7	720.6
4	35	213.5	724.8	9	45	201.1	724.3
4	45	205.1	703.7	9	55	198.3	728.3
5	5	152.1	930.5	10	30	134.6	913.1
5	10	208.8	835.2	10	35	140.5	897.3
5	20	225.4	748.6	10	40	141.9	881.1
5	25	207.9	715.9	10	45	153.0	883.8
5	30	222.8	718.8	10	55	154.9	884.0
5	40	219.8	695.8	10	65	153.6	880.0

III. Discussion of Results and Some Related Experiments

That the combined use of tetramethylthiuram mono- or disulfide and diphenylguanidine should form a molecular compound by the reduction of hydrogen sulfide produced during the vulcanization process has already been discussed in the preceding report. The same reaction may happen in this guanidine-disulfide mixture, thus:

I



To prove whether the equation above is possible, experiments were carried out to decide the question whether they form a molecular compound when hydrogen sulfide is passed into a solution containing them, and if this is obtainable, what is its accelerating activity.

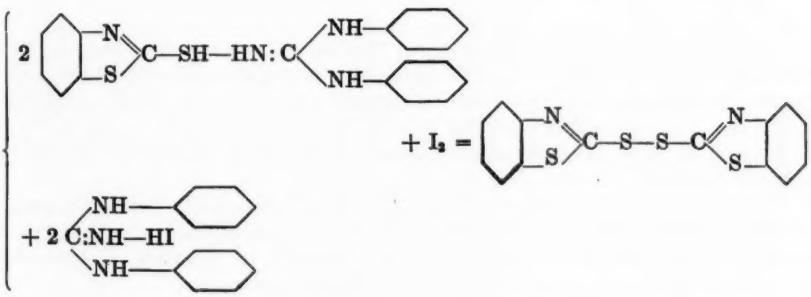
1. Preparation and Detection of the Molecular Compound, Mercaptobenzothiazolediphenylguanidine

When a mixture of 56 per cent of diphenylguanidine and 44 per cent of dibenzothiazole disulfide is dissolved in benzene, and hydrogen sulfide is passed through the solution, a large quantity of a white precipitate is obtained in a short time. This is filtered and recrystallized twice from hot chloroform. The product is pure white when dried, is composed of colorless needles, melts at 172–173° C., is difficultly soluble in cold water, carbon tetrachloride, benzene, toluene, and petroleum ether, is slightly soluble in hot water and hot benzene, and is soluble in alcohol, acetone, and chloroform. The melting point and the crystalline form of the molecular compound are close to the one described in the preceding report, I.

An iodine titration, made after dissolving 0.2 g. of the product in alcohol, required 3.83 cc. of 0.1372 *N* iodine solution, which is equivalent to 0.0670 gram iodine.

In the iodine oxidation of mercaptobenzothiazolediphenylguanidine, the following chemical change is probable:

II

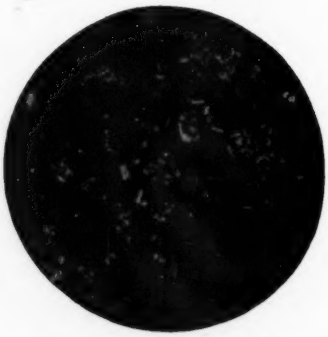


The iodine requirement of the molecular compound, calculated from the above equation, is 0.0671 gram per 0.2 gram which shows a good agreement with the experimental result.

Experimental proofs of the reaction above were made by the following experiments:

(*a*) *Detection of Dibenzothiazole Disulfide.*—The precipitate obtained by the iodine oxidation was filtered, dissolved in aqueous potassium hydroxide, reprecipitated by acidifying with dilute hydrochloric acid, washed, dried, and dissolved in benzene. Addition of cobalt oleate in benzene gave a characteristic greenish blue

Diphenylguanidine



Dibenzothiazole disulfide

Mercaptobenzothiazolediphenylguanidine

Figure 4

coloration of mercaptobenzothiazole (cf. Shimada, *J. Soc. Rubber Ind. Japan*, **6**, 263 (1933)). This is due to the reduction of dibenzothiazole disulfide by potassium hydroxide to form a potassium salt of mercaptobenzothiazole, which is soluble in water and gives the coloration after acidification. The precipitate formed by the iodine oxidation of the molecular compound is proved in this way to be dibenzothiazole disulfide.

(*b*) *Detection of Diphenylguanidine.*—The filtrate obtained after the separation of the precipitate formed by the iodine oxidation was made alkaline with potassium hydroxide, and the white precipitate was dissolved in benzene. Cobalt oleate gave the characteristic purple coloration of diphenylguanidine.

These experiments confirmed the structure of the substance obtained from the mixture of these accelerators by treatment with hydrogen sulfide and showed that this compound is decomposed, as indicated in Equation II, by the iodine oxidation.

Microscopic Test.—Micrographs of the products, shown in Fig. 4, are identical with the ones obtained in the preceding report, I.

These tests give sufficient proof that the substance is a molecular compound, mercaptobenzothiazolediphenylguanidine.

2. Vulcanization Experiment with the Molecular Compound

Compounding and vulcanization were carried out in the same way as in Experiment 4. The molecular compound prepared with hydrogen sulfide and recrystallized from hot chloroform melted at 172–173° C. The mixtures were vulcanized by steam at 30 lbs. pressure per sq. inch. The results are shown in Table VII and Fig. 3.

TABLE VII

VULCANIZATION WITH THE MOLECULAR COMPOUND

Time of Vulcanization (Min.)	Tensile Strength (Kg. per Sq. Cm.)	Elongation (Percentage)	Time of Vulcanization (Min.)	Tensile Strength (Kg. per Sq. Cm.)	Elongation (Percentage)
5	191.3	847.8	25	213.0	670.8
10	225.7	772.0	30	207.3	663.1
15	235.1	732.6	35	207.8	656.3
20	228.2	703.3	45	202.3	650.2

The tensile strength of the undervulcanized rubber (see Fig. 3), was nearly the same as that of Sample 6 in Experiment 4, but it was different from the samples after longer times of vulcanization. This difference may be attributed to the fact that one is a compound and the other is a mixture, and the melting points of these two are widely different.

It is considered that the mixture turns to the molecular compound during vulcanization by the aid of hydrogen sulfide, and it is this molecular compound which increases the acceleration.

Conclusion

The combined use of diphenylguanidine and dibenzothiazole disulfide as a vulcanization accelerator in proper proportions gave a supervulcanization efficiency without danger of scorching; a mixture of 56 per cent of guanidine and 44 per cent of disulfide gave the highest tensile strength, and avoided scorching.

Summary

1. Diphenylguanidine and dibenzothiazole disulfide do not form a molecular compound or eutectic mixture, as judged by their melting and softening point curve.

2. The effects of scorching were studied by the use of various proportions of diphenylguanidine and dibenzothiazole disulfide; the maximum scorching was found with the mixture which had the lowest melting point in the curve.

3. These proportions were also studied for their vulcanizing power.

4. Diphenylguanidine and dibenzothiazole disulfide form a molecular compound through the medium of hydrogen sulfide.

5. This molecular compound was prepared and tested for its vulcanizing properties.

6. The formation, during vulcanization, of the molecular compound, mercaptobenzothiazolediphenylguanidine which takes part in the acceleration, is discussed.

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The Testing of Rubber and Rubber-Like Materials for Oil-Resistance

O. M. Hayden

E. I. du Pont de Nemours and Co., Wilmington, Delaware

Methods of determining the tensile strength, extensibility, elasticity, abrasion-resistance, cutting resistance, and other physical properties of vulcanized rubber are well established. However, less attention has been given to the development of methods of determining its oil-resistance and interpreting the results of such tests.

As applied to rubber and rubber-like products the term "oil-resistance" is defined as their capacity to resist physical changes during or following contact with oils or solvents. The purpose of this paper is to discuss methods for determining the extent of the various changes that occur and to comment on the significance of these changes as related to the performance of the products in service.

Significance of Dimensional Changes.—The most obvious effect of immersing rubber or rubber-like materials in oils or solvents is an increase in volume. This is of course an important property, but it is of less importance than would be inferred by reading many consumers' specifications. Rubber is used as a material of construction because of its extensibility, elasticity, strength, and toughness. If none of these properties was affected by contact with oil, changes in dimensions and in volume would not greatly restrict its use. Obviously, the tendency to increase in volume is a serious shortcoming in rubber that is used for the tube of small diameter oil or solvent hose, but if this were the only shortcoming it could be taken care of by building the hose with a sufficiently great internal diameter to make possible sufficient flow after the rubber had reached its maximum degree of swelling. The percentage of increase in thickness and in volume is of little value in indicating the life of a rubber product, as will be seen from an analysis of the test results on two rubber compounds shown in Table I.

Table I

Effect of Kerosene on Two Rubber Compounds

	Cure (Minutes at 274° F.)	Percentage Increase in Weight	Percentage Increase in Volume	Condition
Compound A[a]	30	270	338	Brittle
	45	222	278	Brittle
	60	202	253	Brittle
	90	176	220	Brittle
Compound B[a]	30	302	372	Flexible
	45	264	325	Flexible
	60	235	289	Flexible
	90	237	292	Flexible

[a] *Compositions:*

	Compound A (Parts by weight)	Compound B (Parts by weight)
Smoked sheet	100	100
Zinc oxide	10	10
Stearic acid	1	1
Phenyl-beta-naphthylamine	2	2
Diphenylguanidine	1	...
Tetramethylthiuram monosulfide	...	2.6
Sulfur	5	0.4

Table I shows the changes in weight and volume that occurred when molded test specimens of these two compounds, 1 × 2 × 0.080 in. thick, were immersed for one month in kerosene at 82° F. The test specimens were weighed before immersion; after removal from the kerosene they were wiped dry with a cloth and weighed immediately. The percentage of increase in volume was calculated according to the formula:

$$\text{Percentage increase in volume} = \frac{\text{Percentage increase in weight} \times \text{specific gravity of sample}}{\text{specific gravity of kerosene}} \qquad (1)$$

If the oil-resistance of these two rubber compounds were judged only by the changes in weight and volume during immersion in kerosene, one would be forced to the conclusion that compound A is better than compound B. However, compound A lost practically all of its strength and toughness during immersion, and at the end of the test it was so tender that it could not be bent on itself without breaking. Compound B, on the other hand, retained its strength, extensibility, and toughness to a considerable degree, and is therefore a more serviceable compound for use in contact with kerosene. These data demonstrate clearly that changes in weight and volume do not indicate the extent of other and more important physical changes that may take place when rubber is in contact with kerosene. In other words, dimensional changes do not parallel changes in other and more important physical properties.

Measurement of Dimensional Changes.—It is extremely difficult to measure accurately the changes in dimensions that occur in rubber during immersion in a swelling medium. Changes in length and width can be measured with a fair degree of accuracy if the specimen has undergone no distortion during immersion, but accurate measurement of thickness after immersion is quite impossible, due to the extreme softness of swollen rubber.

Perhaps the best method of measuring changes in volume during immersion is by water-displacement. This is often referred to as the "Navy Method," and is used in U. S. Navy Department Tentative Specifications for non-metallic gasoline hose, No. 33 H 2, dated June 24, 1932. The necessary data may be quickly obtained with a Jolly or other suitable balance, and the volume changes calculated according to the formula:

$$\text{Percentage increase in volume} = \frac{\text{Water-displacement after test} - \text{initial water displacement}}{\text{initial water-displacement}} \times 100 \qquad (2)$$

Other observers, including the author, have determined changes in volume by measuring changes in weight and calculating the volume changes according to Equation 1 of this paper. This method of calculation requires the assumption that the volume of the rubber after immersion in the solvent is equal to its original volume plus the volume of liquid absorbed. It will give erroneous results if the volume of the rubber itself changes during immersion, due to removal of extractable materials from the rubber by the solvent in which it is immersed. Erroneous results may also be obtained when the liquid in which the rubber is immersed contains two or more components having different specific gravities, because the two components may not be absorbed by the rubber to the same extent. Hence, when swelling tests are conducted in a mixed liquid, the specific gravity of the liquid absorbed may not be the same as the specific gravity of the swelling medium.

The Navy method (water-displacement) is not open to these objections because it measures the percentage of increase in volume directly, and does not involve the

assumptions upon which the calculation of increase in volume from increase in weight is based.

Measurement of Weight Changes.—Test specimens should be wiped dry before weighing, and the time interval between the removal from the swelling medium and weighing should be kept constant, and as short as possible in order to reduce to a minimum the possible error due to evaporation of the swelling medium.

Significance and Measure of Extraction and Sloughing.—Changes in weight and volume should never be taken as criteria of oil-resistance without also taking into consideration the quantity and kinds of material extracted by the swelling medium. The presence of extractable material is indicated by changes in the appearance of the oil or solvent used as the swelling medium. The quantity of extractable matter in natural rubber and in most rubber-like products is not great and is quite constant. However, compounding ingredients are often used which may be extracted in varying degrees by different swelling media.

The amount of matter extracted by a volatile solvent may be measured by evaporating the solvent to dryness and weighing the residue. There appears to be no satisfactory method of measuring the amount of material extracted by a non-volatile solvent.

Many rubber compounds will "slough off," that is, undergo a surface disintegration, when immersed in oils, and deposit fine particles in the liquid. The contamination of the liquid in this manner is often very objectionable. For example, if a gasoline hose tube "sloughs off," the gasoline is discolored, and the particles of rubber may clog screens, etc., causing no end of trouble and delay.

Accurate measurement of the degree of "sloughing off" is quite difficult. One may, of course, weigh the sample after drying out the liquid or weigh the residue that remains after evaporating a volatile liquid. But such tests fail to differentiate between solid particles that "slough off" and soluble material extracted from the compound. One method of differentiation between these two sources of contamination is to stir the test specimen gently in the liquid after completion of the swelling test, strain the liquid, and weigh the dried residue collected on the screen. However, it is believed that the most satisfactory test is to examine the sample carefully during and at the completion of the test, and to determine the extent of surface disintegration by wiping it with a clean cloth or by scraping lightly with a penknife.

Significance of Changes in Physical Properties.—No rubber compound may properly be called oil-resistant unless its strength, resilience, toughness, etc., are maintained to a high degree during contact with the oils to which it will be exposed in service.

In considering methods for determining changes in these physical properties during contact with oils, it is necessary to differentiate sharply between two types of tests. If the product is subjected to abrasive wear or to other mechanical stresses while immersed in or still saturated with the swelling agent, it seems obvious that tests for changes in physical properties should be conducted immediately after removal of the specimen from the testing liquid. Physical tests conducted at this time may be called "deterioration tests." On the other hand, if the conditions of service are such that the product will be subjected to severe mechanical strain some time after removal from contact with the solvent, it is then desirable that physical tests be conducted after a period of rest following removal from the swelling medium. Tests conducted at this time may be called "recovery tests." Obviously, the rest period should be sufficient to permit volatilization of a considerable portion of the swelling agent.

Most rubber or rubber-like products called upon to resist the action of oils and solvents are subjected to mechanical strains during contact with the oil. In testing for this condition of service, deterioration tests should be applied rather than recovery tests. On the other hand, certain products are used under conditions of service where recovery tests should be applied rather than deterioration tests. An example is tank-loading gasoline hose which is used intermittently and is subjected to the most severe mechanical strains, not while in use, but after having been used and after having had an opportunity to "recover," that is, to lose by volatilization a considerable portion of the gasoline it has absorbed.

The time interval between the removal of the test specimen from the swelling agent and making the test does not necessarily classify the test as "recovery" or "deterioration." For example, a tension test made on a test specimen one hour after removal from gasoline would be classed as a "recovery test," whereas the same test made one hour after removal from lubricating oil would be classed as a "deterioration test," because in the first instance the test specimen has recovered somewhat, due to the volatilization of the gasoline, whereas in the second case no appreciable amount of the lubricating oil has evaporated.

Measurement of Changes in Physical Properties.—There are no testing machines capable of measuring accurately the tensile strength, elongation at break, elastic modulus, tear-resistance, and abrasion-resistance of a rubber compound while it is swollen and wet with a solvent. Consequently, when one wishes to determine the changes in these properties during immersion in a swelling agent, he must rely on manual tests with the aid of such simple tools as the finger-nail, a blunt screw-driver, and a pocket-knife. Such tests are of course incapable of numerical expression, but in the hands of an experienced operator they may be developed to a surprisingly high degree of accuracy. Tensile strength and elongation are estimated by stretching the sample until it breaks. The stiffness or elastic modulus is determined by stretching the swollen sample and making a mental note of the approximate force required to stretch it to a given extent, compared with the force required before immersion. The tear-resistance can be determined with the finger-nail or with a screw-driver, and should be correlated mentally with the grain effect which is aggravated in swollen rubber. Abrasion-resistance can be judged by scraping with a penknife.

If the conditions of service to which the product will be subjected are such that a recovery test is significant, it then becomes practical to apply the conventional machine tests for tensile strength, elongation, modulus, and tear-resistance. It must be borne in mind, however, that the conventional testing machine is not at all well suited for the determination of physical properties of badly deteriorated samples. Hence, if recovery tests are to be of value, the immersion test must be stopped at a moderate degree of deterioration. It is believed that any machine tests for tensile strength are of little value on samples having a tensile strength of less than 500 lbs. per sq. in. Below this point the manual tests are more significant.

Machine abrasion tests are of no value whatever on a sample that has been exposed to swelling agents, because the unavoidable residue of swelling agent in the sample lubricates the abrasive track.

Factors Affecting Oil-Resistance Tests

Effect of Temperature.—All rubber and rubber-like compounds are more rapidly attacked by oils at elevated temperatures than at normal temperatures. It is frequently desirable to conduct tests at elevated temperatures, either for the purpose of duplicating service conditions or to accelerate the test so that the testing

engineer may forecast the performance of the compound in the shortest possible time. The practicability of heat-accelerated tests depends upon the type of composition being tested and upon the solvent. Obviously, compositions that will be subjected in service only to normal temperatures should not be given heat-accelerated tests if their physical properties are seriously affected by elevated temperatures. Neither is it practical to use the heat-accelerated test when studying the effects of volatile or of flammable solvents.

It is often possible to select a non-volatile solvent or blend of solvents that may be used at elevated temperatures to produce effects comparable to the effect produced by immersion in volatile solvents over a long period of time at normal temperatures. Obviously such a test cannot properly be specified until the testing engineer has accumulated sufficient data to prove that the liquid chosen for test purposes at elevated temperatures produces effects comparable to those produced by the liquids that may be encountered in service.

The weight of experimental evidence indicates that heat acceleration is a practical means of forecasting the performance of most compositions in solvents at normal temperatures.

Effect of Time.—The time required to deteriorate rubber in contact with oils is influenced by the size and shape of the test specimen, by the temperature of the test, and by the rate of diffusion of the swelling medium.

Vulcanized rubber usually swells rapidly during the early period of oil immersion and then falls off to a slow but gradual increment, which increment may be responsible for a considerable part of the total swelling.[1]

In any test of the oil-resistance of rubber, the time element is an important factor, and the investigator should avoid conclusions based on tests that are not run for a sufficient length of time to assure that no further appreciable decrease in physical properties will occur.

Effect of Size and Shape of Test Specimen.—Differences obtained in the results with test specimens of various shapes and sizes are greatest during the early periods of immersion, which is to be expected, because the rate and degree of absorption and diffusion of the swelling agent are important factors. It is obvious that a thin test specimen will be more seriously attacked by oil in a shorter period of time than a thick specimen, which emphasizes the fact that test specimens of the same shape and size should be used to obtain comparable results.

Effect of Aging.—The effect of aging is to reduce the oil-resistance unless the rubber is so compounded as to increase in stiffness with aging, in which case the oil-resistance may be slightly improved. Aside from the effect of aging on oil-resistance, it is obviously necessary from a purely commercial point of view to have a good aging compound, to prevent deterioration both before and during service in oil. Many so-called oil-resisting rubber compositions used in the past were notoriously poor agers, but fortunately the modern trend of compounding rubber for oil-resistance has been also to improve the aging qualities.

The testing of freshly vulcanized rubber compositions for their physical properties is conceded to be poor practice, and is particularly to be discouraged in testing for oil-resistance. Test specimens should be allowed several days' rest before immersion, in order to reach an equilibrium approximating that of the condition during service.

Influence of External Mechanical Forces.—The oil-resistance of rubber and rubber-like products is influenced by the amount and type of mechanical forces applied during immersion. These forces may be static or dynamic, and the composition may be subjected to compression or extension, or both. When the swell-

ing of rubber is restricted by mechanical pressure, the amount of oil absorbed is naturally reduced. When the composition is in motion or in a strained condition, the rate of oil diffusion and of absorption increases.

The scope of this paper is not broad enough to discuss the effect of these mechanical forces in a manner worthy of their importance. They are mentioned only in order to suggest to the testing engineer that, in establishing his performance tests, he should use such test methods as will give results that can be interpreted in terms of oil-resistance under service conditions.

Effect of Quality of Swelling Media.—Not only do different oils and solvents affect rubber and rubber-like compounds in a different manner and to a different degree, but variations in the quality of a given type of oil or solvent often have a marked effect on the test results, and this is particularly true of petroleum products, as was shown by Hayden and Krismann[2] in a study of the effect of immersing a DuPrene compound in various types of crude and refined petroleum products. In this article it was shown that a Pennsylvania crude oil, which consists largely of saturated aliphatic hydrocarbons, caused the DuPrene stock to swell much less than did the Midcontinent crude oils, which are somewhat unsaturated. Coastal crude oil, which is still more unsaturated, and is composed largely of aromatic (naphthenic) hydrocarbons, caused more swelling of the DuPrene compound than did either the Midcontinent or Pennsylvania crude oils. Variable results were also shown with motor fuels and lubricants from different sources. It is therefore very important to use solvents of known source and quality when testing the oil-resistance of rubber and rubber-like compositions.

Summary

The technic of testing the oil-resistance of rubber and rubber-like materials is less accurate than that for many other qualities. It is impossible to obtain exact measurements of the most significant changes that occur during immersion in a swelling medium. The problems facing testing engineers are to develop observation and manual tests which will supplement machine tests, to develop accelerated tests that can be correlated with service conditions, and to interpret test results in values which will demonstrate the performance of these products in oil or solvent service.

References

[1] Scott, "The Swelling of Vulcanized Rubber in Liquids," *Trans. Inst. Rubber Ind.*, **5**, 95 (1929); RUBBER CHEM. AND TECH., **3**, 3 (1930).

[2] Hayden and Krismann, "Effect of Oils and Chemicals on DuPrene Compounds," *Ind. Eng. Chem.*, **25**, 1219 (1933); RUBBER CHEM. AND TECH. **7**, 393 (1934).

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Selection and Use of Age Resistors in Rubber Compounds

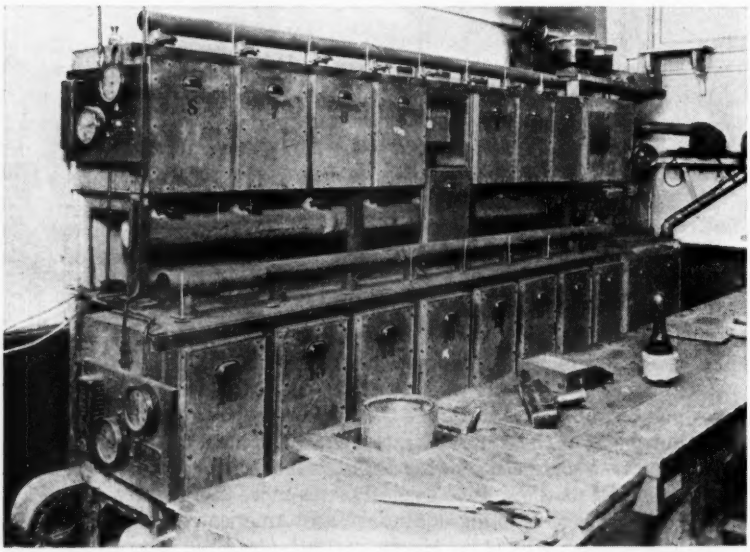
RICHARD A. CRAWFORD, The B. F. Goodrich Company, Akron, Ohio

THE early development of the rubber industry was handicapped by two serious defects in rubber articles. They were not stable to temperature changes, and they deteriorated rapidly with age. Although the process of vulcanization corrected the first difficulty, rapid deterioration with age was common until the discovery of certain organic accelerators, such as *p*-aminodimethylaniline, the aldehydeamines, and mercaptobenzothiazole. Prior to these discoveries a number of materials had been patented for the purpose of improving the age-resisting properties of rubber, but many of them were of little merit and most of the others possessed some accelerating value, a fact which was not appreciated at the time. Typical of the more useful early patents for age-resisting materials are American patents by Murphy in 1870 (*15*), Moore in 1901 (*14*), and Martin in 1922 (*12*), and the German and English patents of the Ostwalds in 1908 and 1910 (*19*, *20*). Murphy patented phenol, cresol, and cresylic acid, either added to the uncured stock or as dipping solutions for vulcanized articles for the purpose of improving their resistance to aging. Moore used reducing agents, including hydroquinone, pyrogallol, and *p*-aminophenol hydrochloride, to preserve the adhesive properties of rubber cements. Martin suggested aniline and other organic bases as a surface treatment for vulcanized articles. The Ostwalds also recognized the beneficial effects of aniline on rubber and stated that it could be added at any convenient stage of manufacture. (It is interesting to note that these inventors considered that addition of aniline to uncured stock or dipping the cured article in aniline were equivalent, and they, therefore, evidently did not recognize the accelerating effect of aniline.)

The beneficial effect of certain organic accelerators on ag-

ing has also been recognized and has been the basis of a number of patents. For example, *p*-aminodimethylaniline was used commercially as early as 1912, although never patented. Later a large number of compounds were patented as accelerators which gave to rubber age-resisting properties. Among these appeared patents for nitro compounds and aromatic amines in 1917–19 (*2*, *13*, *18*); for reducing agents such as hydroquinone for diminishing tackiness of light colored, dry-heat-cured articles in 1921 (*10*); for aldehyde-amines in 1922 (*5*); and a series of patents covering mercaptobenzothiazole and its derivatives.

Until ten years ago the recognized method of producing



BATTERY OF GEER AGING OVENS

good-aging rubber lay in the choice of the proper accelerator. Since not all accelerators produce this effect, the choice was decidedly limited. Some accelerators which imparted good aging conferred on rubber other properties, such as undesirable rate of cure, toxicity, etc., which had to be accepted along with superior aging properties. This method was not an ideal solution of the aging problem, and it was left to later investigators to find means of controlling aging and curing properties independently.

In 1924 Winkelmann and Gray (*23*) secured a patent on nonaccelerating aldehyde-amine condensation products as age resistors. This was followed in 1927 by a patent to Cadwell (*6*) covering the aldehyde-amine condensation products made in the presence of acids. With the introduction of these materials, independent control of age-resisting and cur-

ing properties became possible. For the first time accelerators could be chosen to produce the desired rate of cure and physical properties without regard to their possible effect on the aging of rubber articles. This resulted almost immediately in great improvement in the quality of rubber goods because the deficiencies of accelerator-sulfur combinations which produced high quality but were known to produce poor aging could now be corrected by the addition of age resistors. During the past ten years a great many materials which will retard the deterioration of vulcanized rubber on aging have been placed on the market; the principal ones are included in the classes of: (*a*) phenols, (*b*) aminophenols, (*c*) mono- and diprimary aromatic amines, (*d*) mono- and disecondary aromatic amines, (*e*) aldehyde reaction products of aromatic amines, and (*f*) ketone reaction products of aromatic amines. It should not be assumed, however, that all chemical compounds in these classes are age resistors.

The beneficial effects of age resistors can be demonstrated by aging under normal storage or service conditions. However, the rapid development of the rubber industry in general and of age resistors in particular has made imperative more rapid testing than is possible by natural aging alone. For this reason accelerated aging tests have been employed to an increasing extent for the comparison of resistance to aging of rubber compounds. Of these tests the Geer and Evans oven (*8*, *9*) and the Bierer and Davis oxygen bomb (*1*) are the most widely used.

In the attempt to obtain quantitative information, measurements have been made of specific physical properties of rubber stocks before and after aging. Change of tensile strength was the first criterion to be utilized and is still used more extensively than any other in measuring the effects of aging. That an age resistor actually does improve resistance to aging, as judged by tensile tests, under both natural and artificial aging conditions is well known (*4*).

In recent years it has become recognized that the effect in improving the tensile strength of aged cured rubber is only one of the factors to be considered in selecting an age resistor. Some other factors governing the choice are: (*a*) its effect on processing properties, (*b*) its tendency to bloom, (*c*) its effect on properties other than tensile strength of unaged cured rubber, and (*d*) its effect on properties other than tensile strength of aged cured rubber.

It is the purpose of this paper to present information concerning the proper choice and use of age resistors by the rubber compounder. Data are presented to illustrate effects to be gained by the use of age resistors rather than to serve as a critical comparison of specific materials. The age resistors mentioned in the tables should be considered as representative of the chemical types to which they belong. However, members of any given class vary among themselves in

activity, and it should not be assumed that they are all of equal value for any given purpose.

In studying the behavior of age resistors, reliable and valuable generalizations can frequently be drawn from a large number of qualitative observations of a wide variety of compounds which would be missed entirely if consideration were given only to a few quantitative experiments in a narrow field. In order that rubber compounders may have for their selection and use of age resistors the benefit of this broader experience, conclusions based on numerous qualitative comparisons are included with others for which detailed data are presented.

Effect on Processing Properties

The addition of any material to a rubber compound may affect its properties in both the cured and uncured states. One of the most important factors in influencing the ready acceptance of a rubber compounding ingredient is the manner in which it affects processing properties. Tack, plasticity, scorching tendency, and bloom are factors which must be given consideration if useful articles are to be made from a rubber compound. Of these, plasticity and scorching tendency are perhaps the most important from the processing standpoint. It is proposed, therefore, to discuss in some detail the effect on these properties of several representative age resistors.

Table I. Increase in Plasticity[a] of Smoked Sheet Rubber Produced by Addition of Various Materials

Material Added	Plasticity Changes Produced by: 1%	2%	3%
Aldol-α-naphthylamine	0.2	2.3	4.6
Mixed ditolylamines	−0.5[b]	0.5	1.4
Phenyl-β-naphthylamine	−0.7	0.0	1.1
Di-β-naphthyl-p-phenylenediamine	2.4	1.8	1.2
Synthetic product A[c]	4.6	6.2	10.0
Crude corn oil	6.6	9.5	12.3
Pine tar oil	7.5	10.6	13.7
Crude lauric acid	2.8	13.0	14.2
Natural rosin oil	1.9	6.3	10.7
Liquid jet rosin	3.7	7.7	11.2
Rosin (K gum)	5.7	12.0	18.1
Zinc stearate	0.5	12.2	24.2
Zinc laurate	10.6	15.3	26.5
Oleic acid	15.5	19.7	19.5

[a] Plasticity measurements were all made on the Goodrich plastometer at 100° C.; highest figures denote greatest increase in plasticity.

[b] Minus sign preceding a figure indicates stiffening; the average plasticity for smoked sheet rubber without softener is about 10 units.

[c] A mixture of diarylamino compounds, largely diphenylamine.

Plasticity. The desired plasticity characteristics of rubber compounds are usually secured by addition of the proper kind and amount of one or more softening agents. A number of claims have been made for the valuable softening action of various age resistors. While it is true that they are in some cases softeners for rubber, it is equally true that some are rubber stiffeners. Age resistors, in general, are not

outstanding in softening value, and in the concentrations generally recommended for rubber compounds (about one per cent) the resultant change in plasticity is frequently negligible. Certainly, equal softness can be obtained at lower cost by using any one of a number of common rubber softeners. Table I shows the net change in plasticity of smoked sheet rubber produced by the addition of various percentages of several commercial softeners and age resistors.

The net plasticizing effect of a softener in a rubber compound depends not only upon its softening action on the rubber but also upon its effect upon the subsequent rate of breakdown during further processing. Table II shows that if one per cent of age resistor is added to smoked sheet on a roll mill, the increase in plasticity of the rubber at the end of the mixing is less than when rubber is masticated an equal length of time without the addition of age resistor. Such a result might be expected, since recent data published by Cotton (*7*) and by Busse (*3*) indicate that breakdown of rubber on a mill is due to the effect of oxygen, and age resistors protect rubber from attack by oxygen. Obviously, this effect of age resistors on the rate of breakdown of rubber tends to neutralize their softening action, so that the net effect of small amounts of most of them is slight. The effect on aging properties, rather than on processing, should be considered in choosing these materials. An ideal age resistor, from the compounder's standpoint, would be one which has no effect on processing properties because no other changes in compound would be necessitated by its use.

TABLE II. EFFECT OF AGE RESISTORS ON RATE OF BREAKDOWN OF SMOKED SHEET RUBBER

(2 kg. rubber milled 3 minutes on a 30.48 × 60.96 cm. mill, 1 per cent age resistor added, milling continued another 15 minutes; samples taken after 3 and 8 minutes; difference between these figures represents effect of 5-minute milling with or without age resistor.)

AGE RESISTOR	RELATIVE PLASTICITIES[a] AT 100° C.		
	3 min.	8 min.	Difference
None	16.9	51.8	34.9
Aldol-α-naphthylamine	10.4	41.0	30.6
Phenyl-β-naphthylamine	13.6	42.0	28.4
Acetaldehyde-aniline reaction product	10.0	23.9	13.9
Phenyl-α-naphthylamine	11.1	40.7	29.6
Phenyl-α-naphthylamine + *m*-toluylene-diamine and stearic acid	9.7	25.5	15.8

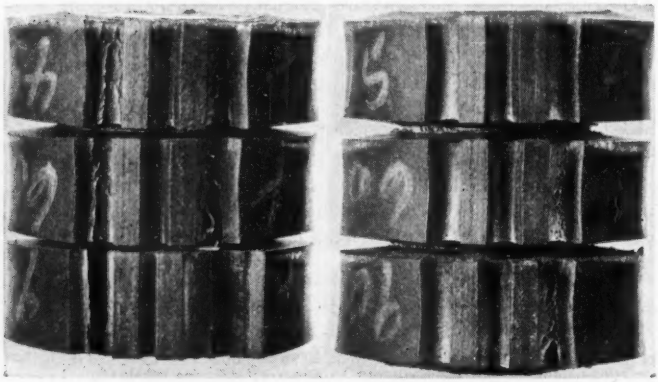
[a] All plasticities measured on Goodrich plastometer; highest figures represent greatest plasticity.

ACTIVATION OF ACCELERATORS. Of the other factors governing the acceptability of rubber compounding ingredients, their effect on scorching and on bloom are, perhaps, next in importance to their effect on plasticity. Since scorching is, in fact, vulcanization, anything which tends to increase the rate of cure of a compound generally increases its scorching tendency at processing temperatures. Acid accelerators are activated by bases, and, since most age resistors are basic, they activate acid accelerators, as is to be expected.

The degree of activation depends upon the kind and amounts of accelerator and age resistor used. Primary aromatic amines, and more particularly primary aromatic diamines, such as 2,4-diaminodiphenylamine and *p,p'*-diaminodiphenylmethane, are powerful activators for such accelerators as mercaptobenzothiazole, whereas diaryl amines, in general, are less active.

With the exception of the primary aromatic diamines, most age resistors do not have much accelerating value in their own right. Moreover, since they are usually bases, their effect on acceleration with basic accelerators is probably merely additive, and they are therefore not likely either to give increased trouble with scorching or upset the rate of cure of the compound.

In Table III are presented data which show the activating



Effect of Cure on Flex Cracking of Pullman Treads, with and without Age Resistor

Left: without age resistor; right: containing 0.75 per cent phenyl-β-naphthylamine. Both samples were cured, aged, and flexed on a Scott machine under the same conditions. The optimum cure was 45 minutes.

effect of representative age resistors on typical acid accelerators and a typical basic accelerator. Age resistors are not to be recommended for use primarily as activators for accelerators, however, because cheaper and more efficient materials are available for that purpose. An ideal age resistor for general use would have no activating effect, and, the more nearly this ideal is approached, other things being equal, the more readily is the age resistor applied by the compounder.

The base recipe for the compound used in Table III is:

Smoked sheet	100
Zinc oxide	10
Sulfur	3
Age resistor	0.75
	113.75

to which were added accelerators and stearic acid as follows:

Accelerator Added	Amount on Rubber	Amount of Acid on Rubber
	%	%
Tetramethylthiuram disulfide (Tuads)	0.2	1
Zinc salt of dimethyldithiocarbamic acid (Zimate)	0.2	1
Mercaptobenzothiazole (Captax)	0.5	2
Heptaldehyde-aniline (Heptene base)	0.3	1

Bloom. Certain age resistors contribute to the blooming of vulcanized rubber compounds. This effect is dependent upon both the specific age resistor and the particular compound in which it is used. The amount of age resistor required to bloom from vulcanized rubber is the resultant of a number of factors, some of which are as follows:

Factor	Favoring Blooming	Favoring Nonblooming
Melting point	Medium (30–150° C.)	Low (less than 30° C.) or high (above 200° C.)
Crystallizing tendency	Ability to crystallize in presence of impurities	Low; prevented or retarded by impurities; resinous or sirupy
Solubility in rubber	Medium	High or very low
Solubility in oils	Medium	High or very low

The properties of typical age-resisting materials are listed in Table IV for substances representing a wide variation of physical properties and chemical constitution. The properties listed above are given in Table IV for each age resistor with the notation B or NB in each case, denoting that the particular property is favorable to blooming or to nonblooming, respectively.

Compounding ingredients other than age resistors may have an important effect on age resistor bloom, if the concentration of the age resistor is near the point above which bloom is to be expected. Other materials—sulfur, some accelerators, fatty acids, soaps, waxes—may increase the tendency of an age resistor to bloom, possibly because of the mutual effect of each material bringing the others to the surface. A smooth film of bloomed material containing age resistor is sometimes desirable, since concentration of age resistor on the surface retards oxidation and the action of light at the point of attack. Oils have a variable effect; usually they decrease tendency to bloom, but, whenever the oil tends to solubilize the age resistor, an increase in blooming may occur. The fact that age resistors bloom when used in high percentages is no more valid argument against their use than the fact that 6 per cent of sulfur on the rubber, for example, will cause bloom is a valid argument against the use of sulfur in nonblooming stocks. In either case knowledge of the material is necessary for its satisfactory application.

Blooming is an elusive effect and must be carefully investigated with reference to specific compounds. Often blooming does not occur until the surface of the stock has been me-

TABLE III. EFFECT OF VARIOUS AGE RESISTORS ON CURING PROPERTIES OF REPRESENTATIVE ACCELERATORS

ACCELERATOR	TEMP. OF CURE °C.	CURE Min.	No AGE RESISTOR	ALDOL-α-NAPHTHYLAMINE	PHENYL-β-NAPHTHYLAMINE	DI-β-NAPHTHYL-p-PHENYLENEDIAMINE	MIXED DITOLYLAMINES	2,4-DIAMINODIPHENYLAMINE	p,p'-DIAMINODIPHENYLMETHANE	PHENYL-α-NAPHTHYLAMINE
			EFFECT ON TENSILE STRENGTH (KG. PER SQ. CM.)							
Tuads	127	10	7	35	7	7	7	309	232	18
		20	295	320	295	281	281	329	346	301
		30	313	302	302	309	295	285	336	309
		45	295	281	285	301	288	288	295	285
		60	279	295	278	294	285	295	302	288
Zimate	115	10	160	200	188	190	183	232	189	162
		20	253	295	239	288	232	236	225	246
		30	278	292	281	304	211	303	246	275
		45	287	309	315	309	253	309	281	295
		60	315	309	327	296	292	336	267	313
Captax	138	10	158	141	113	153	169	225	232	183
		20	229	218	230	211	232	281	274	232
		30	243	243	225	218	253	282	278	239
		45	241	241	232	246	225	272	260	253
		60	218	229	243	253	253	266	260	253
Heptene base	13	10	98	98	120	102	125	155	172	105
		20	169	171	186	204	185	211	248	182
		30	239	239	229	240	243	268	253	226
		45	268	279	265	268	260	264	309	258
		60	267	267	264	274	255	278	281	253
			EFFECT ON ULTIMATE ELONGATION (PER CENT)							
Tuads	12	10	900	788	830	960	853	770	795	840
		20	780	730	753	763	767	683	740	787
		30	730	693	730	730	693	630	707	720
		45	715	690	700	720	697	647	678	703
		60	715	713	712	737	710	653	705	727

Zimate	115	10	895	847	940	855	955	830	770	930
		20	850	823	855	805	835	750	760	840
		30	830	790	840	785	815	775	785	840
		45	813	770	815	760	835	735	775	785
		60	815	755	800	725	780	720	740	785
Captax	138	10	905	870	905	870	853	775	823	873
		20	803	805	840	800	800	710	753	800
		30	785	797	770	780	770	703	740	803
		45	770	757	773	760	733	683	723	787
		60	757	723	780	763	743	663	723	770
Heptene base	138	10	920	930	925	895	945	870	885	975
		20	815	850	810	840	815	790	785	853
		30	790	800	790	785	795	790	765	783
		45	760	790	765	750	770	720	770	787
		60	740	750	750	730	730	715	730	747
			EFFECT ON STRESS AT 500 PER CENT ELONGATION (KG. PER SQ. CM.)							
Tuads	127	10	..	26	..	..	..	56	42	11
		20	55	71	60	56	53	97	77	53
		30	73	84	72	72	84	120	91	77
		45	77	77	70	70	77	116	93	77
		60	63	69	63	61	70	113	91	65
Zimate	115	10	21	21	20	23	14	29	35	18
		20	28	37	29	42	28	48	54	28
		30	35	43	35	46	32	56	46	33
		45	39	56	46	63	33	69	55	41
		60	42	56	49	67	39	84	63	49
Captax	138	10	19	19	18	19	21	35	20	19
		20	35	29	32	33	35	63	56	39
		30	42	35	41	37	42	70	63	39
		45	49	42	42	42	43	84	63	43
		60	50	49	42	44	52	90	63	43
Heptene base	138	10	15	15	15	18	14	21	21	14
		20	28	26	28	32	27	40	43	27
		30	38	38	35	42	34	49	49	35
		45	49	50	46	56	49	64	60	42
		60	56	57	49	70	53	77	70	49

chanically abraded or until the compound has been exposed to indirect light—as through a glass window—or stored in a warm place. Instances are known where no bloom occurred during the first six months of storage but became quite noticeable at the end of a year. The only way to be sure that objectionable bloom is not encountered is to compound the stock intelligently, store various cures under different conditions, and make periodic examinations for bloom.

If objectionable age-resistor bloom is encountered, there are several methods to combat it:

1. Use less age resistor or a different age resistor. Sometimes a mixture of age resistors can be used to advantage to eliminate bloom, at the same time maintaining or even improving the age-resisting properties of the compound.
2. Change the acidity of the compound. Some age resistors bloom at a lower concentration in a basic stock than in an acid stock.
3. Use another accelerator.
4. Eliminate bloom due to other components. Other constituents, even when blooming in only slight amount themselves, will sometimes induce bloom of the age resistor.
5. Change the type or concentration of oils. The type and amount of oils used sometimes change the limiting concentration of an age resistor, possibly because of their solvent action upon it.

Effect on Properties of Unaged Cured Rubber

While the ready acceptance of rubber compounding ingredients depends in large measure upon their effects on processing and curing properties, nevertheless the outstanding reason for using age resistors is that they impart some desirable property or properties to vulcanized rubber. The primary object of using age resistors, of course, is to secure improved resistance of rubber compounds to deterioration on aging. However, research during the past few years has shown that chemicals can be made which will impart other desirable properties. That is, if the proper age resistor is used, properties important in the service life of the rubber are improved even in unaged rubber. These properties are tensile strength (in some cases), quality of overcures, resistance to flex cracking, and resistance to abrasion. As might be expected, the improvement becomes more marked as the age of the cured rubber increases.

Tensile Strength and Modulus. Improved tensile strength and increased modulus are probably due to the accelerating power of the age resistors, or to their activating effect on accelerators, as shown in Table III. Although high tensile strength is usually not the most important property of a rubber compound from a service standpoint, it is a useful one because many specifications contain tensile requirements. Increased modulus is sometimes undesirable.

Overcures. The improvement effected by age resistors in overcured stocks is important from a service standpoint because increased uniformity of cure in thick masses of rubber

TABLE IV. PROPERTIES OF COMMERCIAL AGE RESISTORS AFFECTING BLOOM[a]

AGE RESISTORS	MELTING POINT °C.	CRYSTALLIZING TENDENCY	SOLUBILITY IN RUBBER	SOLUBILITY IN OILS	MAX. PERCENTAGE NONBLOOMING IN PURE GUM STOCK	EFFECT OF OILS IN COMPD. ON BLOOMING TENDENCY
Aldol-α-naphthylamine	Not definite; NB	None, resinous; NB	High; NB	High; NB	Above 5	Increase
Phenyl-α-naphthylamine	62; B	Low; NB	Medium; B	High; NB	3	Decrease
Phenyl-β-naphthylamine	108; B	High; B	Medium; B	Medium; B	1	Decrease
Ditolylamine	Low; NB	None, liquid; NB	High; NB	High; NB	Above 5	None
Di-β-naphthyl-p-phenylenediamine	235; NB	High; N	Very low; NB	Very low; NB	Above 5	Increase
Synthetic product A	Low; NB	None, sirupy; NB	Medium; B	High; NB	3	Decrease
Synthetic product B[b]	Low; NB	None, sirupy; NB	High; NB	High; NB	Above 5	None
Diaminodiphenylmethane	93; B	Low; NB	Medium; B	Medium; B	1	Decrease
Diaminodiphenylamine	127–134; B	High; B	Low; B	Low; B	1	Decrease

[a] B = favorable to blooming; NB = favorable to nonblooming.
[b] A mixture of trimethyldihydroquinoline and its polymers.

can be obtained in commercial practice. In other words, bad effects due to overcure at the surface of thick articles can be reduced. It appears obvious that this will result in improved abrasive wear in such articles as tires and conveyor belts, and improved flexing life of belt and tire carcasses.

FLEXURE CRACKING. Nellen (*17*) noticed that certain age resistors improved resistance to flexure cracking of tires. This property of age resistors is now regarded as of the highest commercial importance. The factors which appear to be more or less definitely involved in flex cracking are oxidation, cure, pigment dispersion, inclusion of dirt or other foreign material, and grade of rubber used. Other factors of importance are pigment loading, acceleration, type and concentration of reclaim, and softeners. That oxidation is a factor in flexure cracking has been shown by Neal and Northam (*16*), and Jones and Craig (*11*) have shown that certain age resistors reduce this tendency. The effect of cure is shown by the experience of several years with flex cracking tests of tread compounds which indicates that increasing cure beyond the optimum tends to decrease flex cracking resistance. The influence of pigment dispersion on flexure cracking is shown by tests of well-mixed *vs.* poorly mixed batches of the same compound:

The sample, cured in a special mold, is 15.2 × 20.3 × 1.3 cm. and is tapered at the ends. It is backed by a piece of heavy frictioned fabric. There are three crosswise grooves about 0.4 cm. deep and 0.65 cm. apart. Strips 2.54 cm. wide are cut lengthwise which, when bent, resemble a section that might be cut from a tire. These 2.54-cm. strips are flexed on the Henry L. Scott belt flexing machine over a 3.18-cm. pulley. The rate of flexing is 12,600 or 10,000 flexures per hour, depending upon which of two machines is used.

It has been found that this test will give consistent results which generally check road tests on tires within reasonable limits, and will allow fairly accurate estimation of the influence of various factors in flex cracking. Table V shows the results of this investigation.

The presence of dirt and other foreign material affects flex cracking resistance, as indicated by the fact that cracking usually starts, both in road-tested tires and in laboratory samples, at the interface between such materials and rubber (cf. Street, *21*).

That the grade of rubber influences flex cracking is shown by Table VI, which gives results of tests on the same compound with different rubbers.

The statement that pigment loading probably affects flex cracking of treads is based on factory experience which has shown flex cracking resistance to vary as carbon black loading is changed. Experience has shown too that, other things being equal, the resistance to flex cracking of tire treads depends upon the accelerator used.

TABLE V. EFFECT OF PIGMENT DISPERSION ON FLEX CRACKING OF UNAGED TREAD STOCK

(Compound is intermediate-grade tread and contains 0.75 per cent phenyl-β-naphthylamine on the rubber; Scott machine test)

COMPOUND	TEMP. OF MILL ° C.	NO. OF FLEXURES TO CAUSE FIRST CRACKING	OPINION OF TEST OPERATOR
(1) Poor mix[a]	60	28,560	Small cracks in grooves; worst of group
(2) Poor mix	Cold	33,750	Small cracks in grooves; better than (1)
(3) Good mix[b]	60	47,444	Very small cracks and pinholes in grooves; better than (2)
(4) Good mix	Cold	63,745	Few pinholes in grooves; best compound of group
(1) Poor mix	60	28,560	Crack across groove; worst compound of group
(2) Poor mix	Cold	39,757	Cracks in grooves; better than (1)
(3) Good mix	60	49,343	Cracks in grooves; better than (2)
(4) Good mix	Cold	76,552	Small cracks in grooves; best compound of group

[a] Mixing designed to give poor pigment dispersion.
[b] Mixing designed to give good pigment dispersion.

TABLE VI. EFFECT OF KIND OF RUBBER ON FLEX CRACKING OF UNAGED TREAD STOCK

(Diphenylguanidine-hexamethylenetetramine used as accelerator; Scott machine test)

KIND OF RUBBER	NO. OF FLEXURES TO CAUSE FIRST CRACKING	APPEARANCE AFTER FLEXING
(1) Blend of amber and smoked sheets	417,698	Good
(2) Smoked sheets	319,762	Not as good as (1)
(3) Rolled brown	278,978	Much worse than (1) or (2)

Microscopic examination of reclaim-rubber mixtures has shown that most reclaims do not dissolve in or flux with rubber but disperse in small particles as a pigment does. A lumpy reclaim or one which disperses poorly would, therefore, be expected to act like dirt or poorly dispersed pigment.

In testing for the effect of age resistors on flex cracking it is important to use clean, high-grade rubbers, and to secure good pigment dispersion.

ABRASION. Not much information is available on the effect of age resistors on resistance to abrasion of rubber compounds. Claims have been made that certain age resistors have a large effect in improving tread wear. Preliminary tests have failed to show great improvement due to age resistors but have indicated that some improvement can be expected when age resistors are used. Laboratory data have been obtained for phenyl-β-naphthylamine on several machines, some of which (notably the Bureau of Standards type) seem to give results agreeing with road test data. Comparison on this machine of a typical high-grade tread accelerated with the aldehyde-amine accelerator Pullman, with and without phenyl-β-naphthylamine, at optimum cure are shown below. The time of cure was 60 minutes at 146° C., and 0.75 per cent of age resistor on the rubber was used:

Age Resistor	Vol. Loss per 1000 Revolutions of Abrasive[a]	Relative Mileage Indicated
	Cc.	
None	4.56	100
Phenyl-β-naphthylamine	4.32	106

[a] Average of two or more tests.

These data indicate that a slight improvement in abrasive resistance may be expected in the presence of an age resistor even when the tread has not been aged.

Effect of Age Resistors on Properties of Aged Cured Rubber

The beneficial effects of age resistors become more marked as the samples are aged. Properties of aged rubber compounds affected by the presence of age resistors are tensile strength and elongation, modulus, flex cracking resistance, abrasion resistance, and flexing life of tire and belt carcasses.

Tensile Strength. The maintenance of tensile properties of aged rubber was the first observed effect and is now so well known that it is not necessary to discuss it in detail. In general, age resistors are effective with either acid or basic accelerators, and the degree of protection depends upon the chemical nature of the age resistor. Primary diamines (*m*-toluylenediamine, *p,p'*-diaminodiphenylmethane, 2,4-diamino diphenylamine) are generally ineffective from the standpoint of preserving tensile strength. Aldehyde-amines are somewhat more effective and in high concentration (3 to 5 per cent) compare favorably with the best age resistors. Secondary amines (di-β-naphthyl-*p*-phenylenediamine, mixed ditolylamines, phenyl-β-naphthylamine) are very effective preservatives of tensile strength in both the bomb and oven tests.

Table VII. Effect of Phenyl-β-naphthylamine on Flex Cracking Resistance of a Tread Compound Unaged and Aged in the Geer Oven

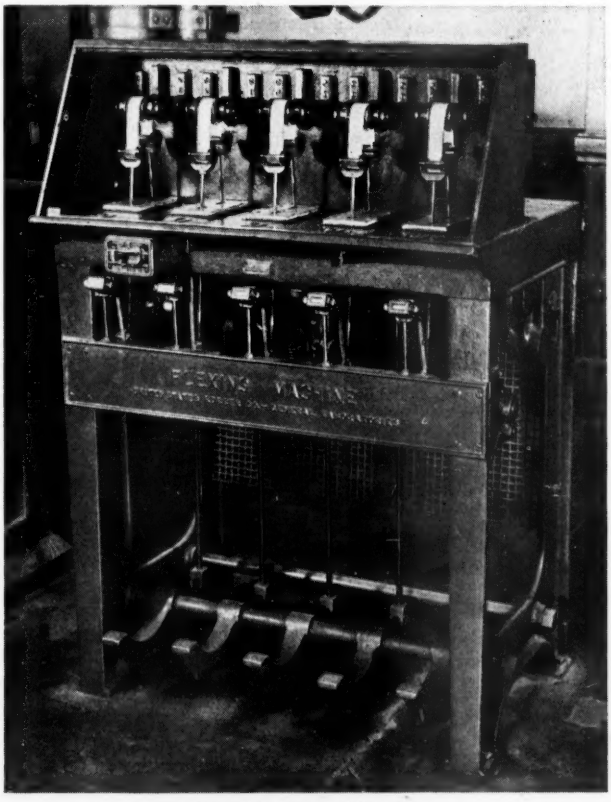
(Diphenylguanidine-hexamethylenetetramine tread; Scott machine test; cure, 55 minutes at 146° C.)

Age Resistor	Aging Period	No. of Flexures to Cause Cracking	Appearance after Flexing
	Days		
None	0	21,669	Fair, cracks in grooves
	2	17,404	Poor, cracks in grooves
	4	11,549	Bad, cracks in grooves
	7	5,963	Very bad, cracks in grooves
Phenyl-β-naphthylamine (0.5% on the recipe)	0	27,056	Good, pinholes in grooves
	2	19,188	Good, pinholes in grooves
	4	17,136	Good, pinholes in grooves
	7	16,184	Good, pinholes in grooves

Flex Cracking. The effect of age resistors on the flex cracking resistance of tread stocks is also more striking after aging. Seven-day Geer-oven aging roughly quadruples the tendency of a diphenylguanidine-hexamethylenetetramine tread stock to crack in the absence of age resistor. If 0.5 per cent phenyl-β-naphthylamine is added to the compound, the

cracking tendency after 7-day Geer-oven aging is less than double that of the unaged stock. This comparison is shown in Table VII.

Some chemicals of doubtful value before aging will increase flex resistance after aging. *p,p'*-Diaminodiphenylmethane has some value after aging but none before; and di-



SCOTT FLEXING MACHINE

β-naphthyl-*p*-phenylenediamine has value in aged stock but none in unaged stock.

The comparison of flexing properties of various compounds by means of the Scott belt flexing machine as described above is time-consuming because it is necessary to test a relatively large number of samples, and the number of samples which can be tested at one time is not great. For these reasons some comparisons have been made on the Rubber Service Laboratories (R. S. L.) flexing machine. This machine has four wheels on a single, motor-driven shaft. These wheels are approximately 25.4 cm. in diameter and about 2.54 cm.

TABLE VIII. EFFECT OF AGE RESISTORS ON FLEX CRACKING RESISTANCE OF AGED AND UNAGED TREAD COMPOUNDS

(R. S. L. machine test)

COMPOUND	TEMP. OF CURE °C.	CURE Min.	1% AGE RESISTOR ON RUBBER	No. OF FLEXES Unaged	No. OF FLEXES Aged	RATING Unaged	RATING Aged
Polybutyraldehyde-aniline (Pullman) tread, 43% black on rubber	146	45	None	1,250,000	350,000	8.50	10.00
			Phenyl-β-naphthylamine	1,250,000	350,000	0.33	1.25
			Synthetic product A	1,250,000	350,000	1.30	1.25
		75	Phenyl-β-naphthylamine	1,250,000	350,000	2.00	3.00
			Synthetic product A	1,250,000	350,000	1.25	3.75
Polybutyraldehyde-aniline (Pullman) tread, 45% black on rubber	146	60	None	2,800,000	120,000	10.00	10.00
			Phenyl-β-naphthylamine	3,000,000	750,000	0.75	1.50
			Aldol-α-naphthylamine	3,000,000	750,000	9.50	6.25
			Mixed ditolylamines	3,000,000	750,000	2.75	3.25
			Di-p-tolylamine	3,000,000	750,000	1.00	1.50
			Synthetic product A	3,000,000	750,000	3.00	2.25
			Synthetic product B	3,000,000	750,000	3.00	3.50
			1,8-Naphthylenediamine	1,700,000	240,000	10.00	10.00
			Di-β-naphthyl-p-phenylenediamine	2,200,000	750,000	10.00	6.50
			2-Mercaptobenzimidazole	3,000,000	350,000	8.50	10.00
Mercaptobenzothiazole tread, 40% black on rubber	138	45	None	4,000,000	1,000,000	5.50	10.00
			Phenyl-β-naphthylamine	4,000,000	1,000,000	0.50	2.00
			Synthetic product A	4,000,000	1,000,000	1.00	2.00
			Phenylcumylamine	4,000,000	1,000,000	0.50	2.00
			Di-p-tolylamine	4,000,000	1,000,000	4.25	3.00
			Synthetic product B	4,000,000	1,000,000	2.00	4.50

wide. In each wheel are twelve slots in each of which is fitted a molded sample of special design. The samples project from the wheels 1.9 cm. and, when rotated, strike two smooth idler pulleys and are thereby flexed 1050 times per minute.

Experience has shown that stocks containing a high percentage of carbon black are perhaps the most suitable for flex testing with this machine. The failure of the samples extends through a range from tiny pinholes through checks and cracks to complete breaks. It is not unusual for a good tread stock to require as many as 4,000,000 flexures before cracking through. Four samples of each stock are tested at one time. Comparisons of various stocks are based on

TABLE IX. EFFECT OF AGE RESISTOR ON THE RESISTANCE TO ABRASION OF AN AGED TREAD STOCK[a]

(Bureau of Standards type machine[b])

0.75% AGE RESISTOR ON RUBBER	AGING PERIOD	VOL. LOSS PER 1000 REVOLUTIONS OF ABRASIVE[c]	RELATIVE MILEAGE INDICATED
	Days	*Cc.*	
AGED IN GEER OVEN			
None	0	4.56	100
Phenyl-β-naphthylamine	0	4.32	106
None	7	4.53	101
Phenyl-β-naphthylamine	7	4.00	114
None	14	5.08	90
Phenyl-β-naphthylamine	14	4.08	112
None	21	6.43	71
Phenyl-β-naphthylamine	21	5.12	89
AGED IN BIERER BOMB			
None	24	11.55	40
Phenyl-β-naphthylamine	24	6.46	71
None	48	20.36	22
Phenyl-β-naphthylamine	48	8.57	53

[a] Pullman tread stock, optimum cure.

[b] This machine uses a medium-coarse aloxite wheel for the abrasive. The sample is clamped to a lever arm and is abraded against the periphery of the wheel. The load is applied by means of weights on the end of the lever arm. The abrasion loss is measured by volume loss in cc. per 1000 revolutions of the abrasive. The conditions of operation for these tests are: size of wheel, 30 × 7.5 cm.; size of sample, 2.5 × 15.25 × 0.95 cm.; speed of abrasive, 60.55 meters per minute; and total load, 5.54 kg.

[c] Each figure is the average of two or more tests.

visual inspection, and good agreement on repeated tests is obtained. This method is made clear by the following examples: Stock A containing no age resistor was flexed with stocks B and C (which contained age resistor) for a total of 1,000,000 flexures. At the end of this time all four samples of A were completely broken or cracked across the face. Such samples are rated 10. Samples with no cracks or pinholes are rated 0, and all others proportionally on a scale between 10 and 0.

In Table VIII are shown the effects of several age resistors on the flex cracking resistance of three tread stocks as measured by the R. S. L. machine. The comparison is on the basis noted above, and the data are therefore roughly quantitative comparisons. Aging was carried out in the Bierer bomb for 48 hours at 70° C. and 21.1 kg. per sq. cm.

oxygen pressure. Aged samples did not receive as many flexures as unaged stock. It was found that, if both unaged and aged stocks were flexed the same number of times, no comparisons could be made, because either the aged stocks would all be rated 10 or the unaged stocks would all be rated 0. Table VIII does not show, therefore, an accurate quantitative comparison of the flex resistance of any single compound before and after aging. It does show, however, the relative value of various age resistors before aging and a similar comparison after aging.

ABRASION RESISTANCE. As mentioned above, the resistance to abrasion of even unaged treads may be better in the presence of an age resistor than in its absence. Table IX shows that, when the tread is aged, this improvement becomes greater.

FLEXING LIFE OF TIRE CARCASSES. Since some air is present in tire cords at the time they are coated with carcass

TABLE X. EFFECT OF PHENYL-β-NAPHTHYLAMINE ON A SUPERAGING COMPOUND (*22*)

(Tensile strength, kg. per sq. cm.; elongation, per cent)

AGE RESISTOR	CURE[a]	ORIGINAL		14-DAY BIERER BOMB TEST		5-HR. AIR-BOMB TEST[b]	
		Tensile strength	Elongation	Tensile strength	Elongation	Tensile strength	Elongation
	Min.						
None	15	269	800	219	750	173	690
	30	279	750	191	710	171	720
	45	274	730	169	690	144	740
	60	270	730	164	680	118	660
Phenyl-β-naphthylamine (1% on rubber)	15	261	800	234	740	199	680
	30	288	750	215	700	193	700
	45	271	720	204	700	176	700
	60	255	720	183	670	160	715

[a] At 138.3° C.
[b] At 127° C. and 5.6 kg. per sq. cm. pressure.

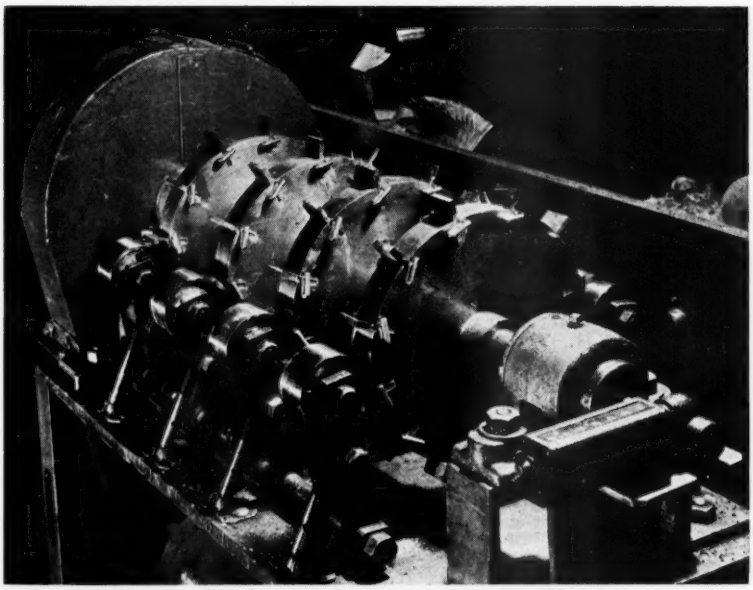
stock, it might be expected that an age resistor would improve the aging properties of tire carcasses and hence the flexing properties of aged tires. An experiment designed to test this effect showed that, although there was no improvement in the unaged stock, 0.25 per cent of phenyl-β-naphthylamine on the rubber doubled the flexing life of a tire carcass after 14 days in the Geer oven. In this test, improvement in flexing life due to age resistor became apparent after 5 days of Geer-oven aging.

SUPERAGING COMPOUNDS

During the past three years a new compounding technic has been developed relating to "superaging" compounds. The essential features of this technic are the use of relatively large amounts of powerful accelerators (usually thiurams), with or without auxiliary acceleration, and relatively small amounts or no added sulfur. They may also contain selenium or tellurium. The outstanding property of compounds pro-

duced by this method is their extraordinary resistance to aging by accelerated tests such as the Bierer bomb, the Geer oven, and the high-temperature autoclave, even in the absence of age resistors. At first glance this property would seem to render superfluous the addition of age resistors to such compounds. That this is not necessarily so is shown by Table X (from data published by the R. T. Vanderbilt Company, *22*) which shows the effect of one per cent phenyl-β-naphthylamine on the rubber in a superaging tire friction.

If the other properties of superaging compounds were as superior as their aging properties, standard compounding practice would be obsolete and superaging compounds would



RUBBER SERVICE LABORATORIES FLEXING MACHINE

find universal acceptance for the production of all kinds of rubber goods. That this has not occurred may be due to too short acquaintance with superaging compounding or to lack of knowledge of the results attainable. It appears more probable, however, that the change in structure which produces the aging properties also produces other fundamental properties differing from those of standard compounds, some of which may not be desirable.

Superaging compounds are not superior in all respects to properly compounded stocks based on standard compounding. They have been found inferior to properly compounded standard type compounds for water resistance, abrasion or flexing under heavy loads, flex cracking, freezing, and resistance to overcure due to sulfur migration in

service. They are little or no better than the best standard type compounds for sun checking and oil resistance. Their comparative value for the latter service depends a good deal on the temperature of test. At elevated temperatures they are usually better, at room temperature they may not be.

TABLE XI. ABRASION RESISTANCE UNDER VARIOUS LOADS OF A SUPERAGING *vs.* A STANDARD TYPE TREAD[a]

(Bureau of Standards type machine; cure, 70 minutes at 138° C.)

COMPOUND	LOAD ON SAMPLE	VOLUME LOSS AT GIVEN AGING PERIOD[b] PER 1000 REVOLUTIONS OF ABRASIVE			RELATIVE MILEAGE INDICATED		
		Original	48 hr.	96 hr.	Original	48 hr.	96 hr.
	Kg.	*Cc.*	*Cc.*	*Cc.*			
Standard	1.81	0.60	0.87	1.25	100	68	48
Superaging	1.81	0.59	0.82	1.17	102	74	51
Standard	4.31	2.21	2.93	4.27	100	75	52
Superaging	4.31	2.97	3.49	5.33	74	63	41
Standard	5.56	2.98	4.25	..	100	70	..
Superaging	5.56	3.81	4.68	..	78	64	..
Standard	6.92	3.64	5.41	7.56	100	67	48
Superaging	6.92	5.50	6.54	9.33	66	55	39

[a] Treads used are A2 and B1 in *Vanderbilt News* (*22*).
[b] Samples aged in Bierer bomb at 70° C. and 21.1 kg. per sq. cm. oxygen pressure.

They are superior to standard type compounds in all kinds of accelerated aging tests and in high-temperature service in air. In the latter service they are of outstanding value and should find their greatest use there.

TABLE XII. EFFECT OF AGE RESISTORS ON FLEX CRACKING RESISTANCE OF A SUPERAGING BELT COVER COMPOUND

(3% age resistor on rubber; R. S. L. machine test)

AGE RESISTOR	UNAGED AFTER 600,000 FLEXURES[a]	AGED 48 HR. IN BOMB AFTER 450,000 FLEXURES[a]
None	2.50	7.25
Phenyl-β-naphthylamine	1.75	1.00
Synthetic product A	5.00	2.00
Di-*p*-tolylamine	1.25	1.50
Phenylcumylamine	2.50	1.00

[a] Indices on same basis as Table VIII.

The abrasion characteristics of a superaging and a standard type tread compound are shown in Table XI for different loads on a Bureau of Standards type abrasion machine. The treads are identical except for acceleration.

TABLE XIII. REASONS FOR USING AGE RESISTORS IN TYPICAL RUBBER STOCKS AND OTHER MATERIALS

MATERIAL	OUTSTANDING SPECIFIC REASONS FOR USING AGE RESISTORS
	RUBBER STOCKS
Pneumatic tire tread	To improve flex resistance and increase resistance to abrasion
Carcass stock	To retard ply separation and lengthen flexing life in service
Solid tire tread	To maintain resiliency and retard tendency to blow out
Passenger tube stock	To improve shelf life
Truck tube stock	To resist high temperatures and prevent melting or stiffening
Air bag stock	To retard embrittlement and minimise the effect of migration of sulfur

TABLE XIII. (*Continued*)

MATERIAL	OUTSTANDING SPECIFIC REASONS FOR USING AGE RESISTORS
Water bag stock	To retard surface cracking and to prevent oxidation of interior surface
Side-wall stock	To retard sun checking and flex cracking
Flaps	To maintain resiliency
Repair stocks	To maintain surface tack and stabilize the curing properties
Black shoe upper	To give nonbrittle shelf aging and nontacky dry heat cures, and to retard flex cracking
White shoe upper	To prevent chalking and cracking
Boot upper	To increase tear resistance and retard flex cracking
Soling stocks	To increase flex and abrasive resistance and flatten cure
Heel stocks	To maintain snap and shelf life
Heel lifts	To maintain elongation and permit bending after aging
Rubber flooring	To retard surface erosion and chalking
Tile	To retard surface erosion and chalking
Matting	To allow a cheaper original stock to be used and still maintain sufficient quality in aged material
Running board stocks	To maintain adhesion to metal
General mechanical stocks	To flatten cure and permit higher curing temperatures
Motor support stocks	To prevent the action of brass on the rubber, maintain resiliency, and maintain adhesion
Belt cover stocks	To retard flex cracking, improve resistance to abrasion, and improve the heat and corrosion resistance of the surface
Belt frictions	To prevent ply separation from building or operating causes
Gum tubing	To prevent softening and cracking
Colored garden hose	To retard chalking and reduce marking
Black hose	To prevent hardening and cracking
Gasoline hose	To maintain flexibility of tightly cured or overcured stock
Fire hose	To prevent development of acid in the tube
Water bottles	To prevent melting or hardening
Bath caps	To prevent melting or hardening
Jar rings	To maintain elongation
Auto topping	To prevent cracking from sunlight
Leatherette	To prevent hardening
Rubber-covered rolls	To maintain original hardness
Tank linings	To make them more corrosion resistant and prevent deterioration by materials such as copper or iron salts
Sheetings	To prevent development of offensive odor
Rubber cements	To maintain tack
Dipped goods	To maintain tensile and resistance to tear
Thread rubber	To maintain elongation and shelf life
Rubber bands	To maintain elongation
Transparent rubber	To insure good aging
Dental dam	To maintain tear resistance
Latex goods	To protect against impurities, to permit dry heat cures, to withstand sterilization
Sponge rubber	Very essential to insure good aging
Wire	To prevent stiffening and shortness of cover
Hard rubber	To minimize discoloration on aging
Sulfur-free stocks	To improve flex resistance and heat resistance
Low-sulfur stocks	To improve flex resistance and heat resistance
Latex-fiber combinations	To prevent resinification and maintain flexibility
Rubber base adhesives	To maintain adhesive properties
	OTHER MATERIALS
Balata	To prevent resinification
Chicle, Pontianak, etc.	To prevent resinification
Rosin	To prevent oxidation which catalyzes deterioration of rubber goods
Rosin-base adhesives	To maintain adhesive properties
Fly stickies	To prevent drying out of the film
Asphalt	To prevent checking, chalking, and cracking
Asphalt paint	To improve weather exposure test
Tire paint	To prevent deterioration of surface to which applied
Top dressing	To prevent deterioration of surface to which applied
Linseed oil	To retard drying
Oil-base adhesives	To maintain adhesive properties
Nitrocellulose and lacquers	To stabilize and prevent embrittlement
Paper	To prevent embrittlement

TABLE XIV. CAUSES AND REMEDIES FOR VARIOUS TYPES[a] OF DETERIORATION OF RUBBER COMPOUNDS

TYPE OF DETERIORATION	CAUSE	REMEDY	COMMENT
1. Loss of tensile strength at ordinary temperatures	Oxidation	Diaryl amines, aldehyde-amines, or ketone-amines	Use any highly active age resistor
2. Decrease in elongation 3. General hardening	Oxidation of rubber, oxidation of free or combined sulfur, or continued cure	Same as 1	Low-melting diaryl amines are especially good
4. Tendency of highly compounded aged stocks to smudge 5. Chalking	Surface oxidation destroying the bonding action of the rubber for the pigments	Same as 1	Waxes, petrolatum, or paraffin also help
6. Development of odor	Oxidation, giving rise to volatile, terpene-like materials	Same as 1	Leave out rosin oil or other readily oxidizable materials
7. Oxidation catalyzed by resinous ingredients, drying oils, deteriorated rubber in compound, deteriorated rubber in contact, metal salts or soaps in compound, or contact with certain metals	The oxidation of rubber is autocatalytic	Same as 1	In contact with easily oxidizable materials, use of age resistor is essential
8. Effect of under- and overcures	.....	Same as 1	Age resistors flatten curing curves and impart better aging to poorly cured articles
9. Effect of curing above optimum temp.	.....	Same as 1	Same as 1
10. Brittle skin formation	High-temp. service, surface oxidation, or surface overcure due to sulfur migration	Aldehyde-amines and certain diaryl-amines	Aldol-α-naphthylamine is recommended
11. Softening by water or steam	Water penetration and reversion	Aldehyde-amines, polyprimary amines	Improvement notable in water bags and steam hose; aldol-α-naphthylamine is recommended

12. Heat deterioration	Oxidation and reversion	Same as 11	.....
13. Oxidation of solvent-swollen rubber	Swelling often affords easier access to oxygen	Same as 11	Effect is seen in gaskets and gasoline hose
14. Oxidation of free or combined sulfur	High free or combined sulfur; overcures	Polyprimary amines	.....
15. Acid formation on oxidized surface	Moist, oxidized sulfur products retained on surface	Polyprimary amines, diaryl amines	Acid deterioration of fire hose cover
16. Effect of inorganic acid materials	Acid hardening of surface	Same as 15	Noted in tank linings
17. Melting or sticky perishing	Oxidation and reversion	Same as 15	Often seen in water bottles and pure gum articles
18. Loss of adhesive bond to metal (brass-copper plate)	Softening at interface	Diaryl amines	.....
19. Copper poisoning of rubber stocks	Accelerated oxidation	Same as 18	.....
20. Flexure cracking	.....	Diaryl amines	Low-melting diaryl amines are especially good
21. Growth of cracks on flexing	.....	Same as 20	.....
22. Cracking originating from dirt nuclei in stock	.....	Diaryl amines	Eliminate dirt from stock
23. Ply separation in service	.....	Same as 22	.....
24. Internal heating by flexure	.....	Diaryl amines + a polyprimary amine	.....
25. Development of tack in dry heat cures	Oxidation	Aldehyde-amines, polyprimary amines	.....

[a] Commercial age resistors which belong to the classifications given in this table are:

Diaryl amines:
- Phenyl-α-naphthylamine
- Phenyl-β-naphthylamine
- Di-β-naphthyl-p-phenylenediamine
- Mixed ditolylamines
- Synthetic product A

Aldehyde-amine condensation products:
- Aldol-α-naphthylamine
- Acetaldehyde-aniline
- Butyraldehyde-aniline

Polyprimary amines:
- Benzidine
- 2,4-Diaminodiphenylamine
- 4,4-Diaminodiphenylmethane
- 2,4-Diaminotoluene

Although flex cracking properties of superaging stocks have proved inferior, both by laboratory flex cracking tests and by road tests on tires, they can be improved by the addition of a properly chosen age resistor. This is illustrated for a superaging belt cover compound (laboratory test) by Table XII.

Choice of an Age Resistor

Age resistors are as specific in their effects on the service qualities of rubber articles as accelerators, and they must be chosen as carefully if the most desirable results are to be obtained. For example, if age resistors A and B are under consideration, and both are of equal value in bomb and oven aging, A may be of great value in increasing resistance to flex cracking, while B is of little or no value; A may have bad staining properties, while B is relatively nonstaining; A may have little value in protection against deterioration at high temperatures, while B is outstanding in this respect. It is necessary, therefore, to determine which properties are desired for a particular article and choose the age resistor which will best maintain them. The choice of the best age resistor for any specific use must depend upon wide experience and critical knowledge of composition and service factors involved.

In Table XIII are listed some of the reasons for using age resistors in typical rubber stocks. The fact that age resistors improve natural, bomb, and oven aging and also minimize the effect of variation in cure is common to all stocks and is not mentioned in the table.

The ways in which rubber may deteriorate are manifold. It is often not possible to correct completely a given difficulty merely by adding an age resistor. It may be necessary to change the accelerator, the accelerator-sulfur ratio, the pigmentation, or the cure. However, the use of an age resistor is always an additional improvement or factor of safety. Types of deterioration which may be remedied by the use of certain classes of age resistors are shown, together with their causes, in Table XIV. It should be understood that not all members of any given group will remedy the type of deterioration given. Age resistors are often specific in their effects, and Table XIV is intended merely as a guide in the selection of classes of age resistors suitable for the purpose in question.

Acknowledgment

The author's thanks are due R. P. Allen and W. L. Semon for aid in the preparation of this paper, especially the sections on bloom and on the causes of and remedies for rubber deterioration.

Literature Cited

(1) Bierer, J. M., and Davis, C. C., Ind. Eng. Chem., 16, 711 (1924).
(2) Boggs, C. R., U. S. Patent 1,296,469 (1919).

(3) Busse, W. F., IND. ENG. CHEM., **24**, 140 (1932).
(4) Cadwell, S. M., *Ibid.*, **21**, 1017 (1929).
(5) Cadwell, S. M., U. S. Patent 1,417,970 (1922).
(6) *Ibid.*, 1,626,784 (1927).
(7) Cotton, F. H., *Inst. Rubber Ind. Trans.*, **6**, 487 (1931).
(8) Geer, W. C., *India Rubber World*, **55**, 127 (1916).
(9) Geer, W. C., and Evans, W. W., *Rubber Age* (London), **2**, 308 (1921).
(10) Helbronner, A., British Patent 142,083 (1921).
(11) Jones, P. C., and Craig, David, IND. ENG. CHEM., **23**, 23 (1931).
(12) Martin, R. B., U. S. Patent 1,410,699 (1922).
(13) Meeus, E. de, *Ibid.*, 1,229,724 (1917).
(14) Moore, L. R., *Ibid.*, 680,387 (1901).
(15) Murphy, John, *Ibid.*, 99,935 (1870).
(16) Neal, A. M., and Northam, A. J., IND. ENG. CHEM., **23**, 1449 (1931).
(17) Nellen, A. H., *Rubber Age* (N. Y.), **24**, 373 (1929).
(18) Ostromislensky, Iwan, U. S. Patent 1,249,180 (1917).
(19) Ostwald, Wolfgang, and Ostwald, Walther, British Patent 10,361 (1910).
(20) Ostwald, Wolfgang, and Ostwald, Walther, German Patent 221,310 (1908).
(21) Street, J. N., IND. ENG. CHEM., **24**, 559 (1932).
(22) Vanderbilt Co., R. T., *Vanderbilt News*, **2** (3), 31, 33 (1932).
(23) Winkelmann, H. A., and Gray, H., U. S. Patent 1,515,642 (1924).

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The Chemistry of Soft Rubber Vulcanization

IV Vulcanizing Agents Other than Sulfur

B. S. GARVEY, JR., The B. F. Goodrich Company, Akron, Ohio

The vulcanizing action of sulfur chloride, m-dinitrobenzene, selenium, tetramethylthiuram disulfide, and benzoyl peroxide has been investigated by the use of a set of tests developed for measuring the degree of vulcanization with sulfur-cured compounds. These tests show that all of these materials are true vulcanizing agents. Comparison of the various vulcanizates with different types of unvulcanized rubber shows that the outstanding characteristic of the vulcanized structure is its resistance to flow under a wide variety of conditions. The vulcanized structure appears to be a composite one which varies with the rate of a reaction catalyzed by the vulcanizing agent, the rate of combination of the vulcanizing agent, the nature of the addition product, and possibly with differences in the nature of the catalyzed reaction.

PREVIOUS papers in this series have covered the development of a set of tests for measuring vulcanization (*10*) and the use of these tests for studying the function of sulfur during vulcanization (*9*), and for comparing vulcanized rubber with unmilled rubber and uncured gas black stocks (*8*). This report covers the use of the same set of tests for a comparison of vulcanization by sulfur with that by other materials generally accepted as vulcanizing agents.

The recipes for the compounds used are as follows:

SULFUR CHLORIDE

Compound 1. First latex crepe was calendered in the laboratory to 0.038 cm. (0.015 inch) and cured in the factory by the vapor process followed by treatment with ammonia.

Compound 2. First latex crepe was calendered and cured (vapor process) in the factory; the sheet was 0.023 cm. (0.009 inch) thick.

COMPOUND 3, *m*-DINITROBENZENE

[Cures: 10, 20, 30, 45, 60, and 120 min. at 142° C. (287° F.)]	
First latex crepe	100
Litharge	10
Gas black	10
m-Dinitrobenzene	3
	123

COMPOUND 4, SELENIUM

[Cures: 15, 30, 60, 120, 240, and 480 min. at 149° C. (300° F.)]	
First latex crepe	100
Vandex (selenium)	28
β-Naphthylamine	4
Paraffin wax	4
Litharge	25
Zinc oxide	50
	211

COMPOUND 5, TETRAMETHYLTHIURAM DISULFIDE

[Cures: 5, 10, 20, and 30 min. at 142° C. (287° F.)]	
First latex crepe	100
Tetramethylthiuram disulfide	4
Zinc oxide	5
	109

COMPOUND 6, BENZOYL PEROXIDE

[Cures: 5, 10, 15, 30, and 45 min. at 135° C. (275° F.)]	
First latex crepe	100
Benzoyl peroxide	4
	104

The dinitrobenzene compound is based on a formula used by Fisher and Gray (*7*); that for selenium is based on a recommendation by Boggs (*5*). The mixing, curing, and testing procedure was the same as that described in detail in the earlier paper (*10*). In Table I are given the testing data for each compound on the uncured stock and on the cured sheet having the highest tensile strength in the range selected.

DISCUSSION OF RESULTS

Comparison of these data with the corresponding data on sulfur compounds, reported in the earlier paper, shows that all of these compounds have undergone the changes characteristic of vulcanization with sulfur. Therefore, according to the criteria used here, the materials tested are true vulcanizing agents.

A comparison of the properties of the different types of vulcanized rubber with each other and with tough crude rubber and uncured gas black stocks shows that all of the vulcanizates have a marked resistance to flow in all of the tests. On the other hand, both the gas black stocks and crude rubber show a comparatively small resistance to flow in one or more of the following tests: hot water, milling, retentivity, thermoplasticity, hysteresis set. With regard to tensile and modulus, both of these types give values as high or higher than do some types of vulcanizate. Uncured gas black stocks, like vulcanized rubber, show low solubility in benzene. In ice water, some vulcanized, high accelerator–low sulfur compounds freeze as badly as crude rubber. It is thus apparent that the outstanding characteristic of the vulcanized structure is its resistance to flow under a wide variety of conditions, especially at high temperatures.

Vulcanization, then, is a reaction which primarily suppresses the flow characteristics of uncured rubber. This change always seems to be accompanied by a marked decrease in solubility and by an increase, to a greater or less extent, in the tensile strength and modulus.

Theoretical Discussion

In these compounds the several properties change at

Table I. Vulcanization Tests on Compounds Cured with Various Vulcanizing Agents

Compound	Cure	Qualitative Tests: Ice water	Hot water	Milling	Solubility	Plasticity Tests: R_{30}	R_{100}	S_{20}	S_{100}	P_{30}	P_{100}	$\frac{P_{100}^2}{P_{30}}$
	Minutes											
1	.....	4	1	5	4	8.1	9.0[a]	4.5	6.3	0.37	0.56	0.85[a]
2	.....	2	1	5	4	Too thin to measure						
3	None	0	0	0	2	46.9	86.0[a]	15.8	65.2	7.4	56	424[a]
	45 at 142° C.[b]	4	1	5	4	6.8	5.8[a]	4.4	5.2	0.30	0.30	0.30[a]
	120 at 142° C.	4	1	5	4	5.7	11.0[a]	4.2	4.8	0.24	0.53	1.17[a]
4	None	0	0	0	0	53.2	93.7[a]	15.6	66.4	8.3	62.2	466[a]
	120 at 149° C.[c]	0	1	3	4	12.6	16.0[a]	5.2	5.9	0.66	0.94	0.13[a]
	480 at 149° C.	4	1	5	4	10.4	12.7[a]	7.5	7.7	0.79	0.98	0.12[a]
5	None	0	0	0	0	38.5	78.6[a]	11.2	46.5	4.3	37.0	318[a]
	30 at 142° C.[b]	3	1	5	4	0	5.7[a]	4.5	3.9	0	0.23	0[a]
6	None	0	0	0	0	75.6	Too soft	51.5	Too soft	39.0	Too soft	Too soft
	10 at 135° C.[d]	3	1	4	4	12.8	10.3[a]	11.8	12.1	1.52	1.26	2.0[a]

[a] Measurements suitable for use without the others. [b] 142° C. = 287° F. [c] 149° C. = 300° F.

Compound	Hysteresis Tests: Set	Modulus at 300%: Kg./cm.²	Lb./in.²	Set Modulus: Kg.	Lb.	Stress-Strain Tests: Modulus at 500%: Kg./cm.²	Lb./in.²	Ultimate tensile: Kg./cm.²	Lb./in.²
1	20[a]	15.5	220[a]	12.7	0.89[a]	77.3	1100[a]	109	1550[a]
2	70[a]	41.9	597[a]	1.7	0.12[a]	91.4	1300[a]	126.5	1800[a]
3	...	...	...	...	...	...	...	...	...
	30[a]	23.9	340[a]	1.28	0.09[a]	91.5	1300[a]	130	1850[a]
	30[a]	30.6	435[a]	1.0	0.07[a]	116	1650[a]	134	1900[a]
4	...	...	...	...	...	...	...	...	...
	45[a]	12.4	177[a]	3.5	0.25[a]	28.1	400[a]	112	1600[a]
	40[a]	11.4	162[a]	3.5	0.25[a]	18.3	260[a]	42	600[a]
5	...	...	...	...	...	...	...	...	...
	15[a]	18.8	267[a]	0.85	0.06[a]	36.6	520[a]	225	3200[a]
6	...	...	...	...	...	...	...	...	...
	40[a]	4.1	58[a]	9.8	0.69[a]	...	...	24	340[a]

[d] 135° C. = 275° F.

different relative rates. Where similar differences were observed in the case of accelerated sulfur compounds, they were attributed to differences in the vulcanized structure depending on the relative rates of two structure-forming reactions, sulfur addition, and a reaction catalyzed by sulfur (*9*). The extension of this explanation to the nonsulfur vulcanizing agents is in agreement with the chemical evidence available.

With sulfur chloride there is an addition reaction which probably results in bridge formation between double bonds of the hydrocarbon (*1*, *11–14*, *19*). With nitro compounds the reagent is destroyed during cure, and there appears to be a small amount of some sort of addition product formed (*2*, *6*, *15*, *18*). Selenium apparently combines to a limited extent with rubber (*3*, *4*). Benzoyl peroxide forms some addition or substitution product and probably also causes some bridge formation by dehydrogenation of the rubber (*17*). Tetramethylthiuram disulfide probably decomposes and liberates a small amount of very active free sulfur (*16*). In all of these cases the amount of addition product is small, either because of low tendency of formation or because of the small amount of reagent available. With sulfur alone there is reason to believe that amounts of combined sulfur up to one per cent are not sufficient to cause more than a very slight vulcanization (*9*). This is probably also the case with equivalent amounts of addition product of these other reagents. It seems probable, therefore, that in all of these cases a catalyzed reaction of the hydrocarbon plays an important part in the vulcanization. In the case of selenium (*4*), nitro compounds (*7*), and benzoyl peroxide (*7*), as with sulfur, there is evidence that this catalyzed reaction is not one involving a change in unsaturation.

Thus there appears to be in all of these cases the probability of at least two reactions: (1) a combination of vulcanizing agent with rubber and (2) a reaction of the hydrocarbon catalyzed by the vulcanizing agent. The product of the combination would, of course, be different with different reagents. Possibly, also, there are differences in the nature of the catalyzed reaction, though in most cases it seems to be one which does not involve a change in the unsaturation of the hydrocarbon. The catalytic activity of the vulcanizing agents undoubtedly depends on the initial composition and also on the stability, and thus varies considerably among the different reagents.

The vulcanized structure seems to be a composite one built up by the catalyzed reaction and modified more or less by the addition reaction.

Literature Cited

(1) Bernstein, G., *Kolloid-Z.*, **11**, 185 (1912).
(2) Blake, J. T., Ind. Eng. Chem., **22**, 740 (1930).

(3) Blake, J. T., *Ibid.*, **22**, 737, 744 (1930).
(4) Boggs, C. R., *Ibid.*, **10**, 117 (1918).
(5) Boggs, C. R., U. S. Patent 1,249,272 (1917).
(6) Bunschotten, E., *Chem. Weekblad*, **15**, 527 (1918); *India Rubber World*, **60**, 559 (1919).
(7) Fisher, H. L., and Gray, A. E., IND. ENG. CHEM., **20**, 294 (1928).
(8) Garvey, B. S., Jr., *Ibid.*, **26**, 434 (1934).
(9) Garvey, B. S., Jr., and Thomson, G., *Ibid.*, **25**, 1292 (1933).
(10) Garvey, B. S., Jr., and White, W. D., *Ibid.*, **25**, 1042 (1933).
(11) Henrichsen, F. W., and Kindscher, E., *Kolloid-Z.*, **6**, 202 (1910).
(12) Henriques, R., *Chem.-Ztg.*, **17**, 634 (1893); **18**, 701, 1155 (1894).
(13) Kirchhof, F., *Kolloid-Z.*, **14**, 35 (1914).
(14) Meyer, K. H., and Mark, H., *Ber.*, **61**, 1939 (1928).
(15) Ostromislensky, I., *J. Russ. Phys. Chem.*, **47**, 1453, 1462, 1467, 1885, 1898, 1904 (1915); Handbuch der Kautschukwissenschaft (K. Memmler), p. 373, S. Hirzel, Leipzig, 1930.
(16) Romani, E., *Giorn. chim. ind. applicata*, **3**, 197 (1921); *Rubber Age* (N. Y.), **10**, 13 (1921).
(17) Rossem, A. van, Dekker, P., and Prawirodipoero, R. S., *Kautschuk*, **7**, 202, 220 (1931).
(18) Stevens, H. P., *J. Soc. Chem. Ind.*, **36**, 107 (1916).
(19) Weber, C. O., *Ibid.*, **13**, 11 (1894).

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Relation of Volume Change to the Mechanism of Rubber Vulcanization

IRA WILLIAMS, E. I. du Pont de Nemours & Company, Wilmington, Del.

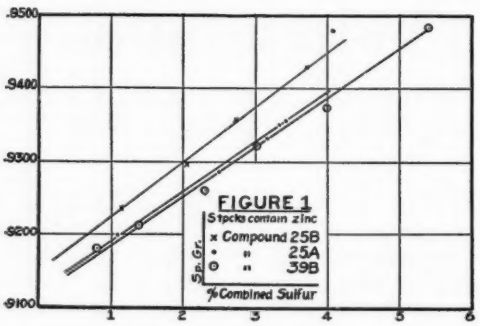
AMONG the many partial explanations of the mechanism of vulcanization, several require a polymerizing action at some step in the process (*1*, *7*, *11*, *14*, *16*, *17*). The actual mechanism of the polymerization is usually not explained, and in certain cases it is probable that the term "polymerization" may be intended to cover some type of phenomena not involving primary valence forces.

A concept of the mechanism of vulcanization involving polymerization is more or less logical following the discovery of the polymerization of butadienes to rubber-like bodies. The polymerization of isoprene which causes a loss of half of the double bonds produces a more or less plastic body, and a further polymerization to an increased molecular weight could conceivably cause the loss of plastic properties which results in vulcanization. This mechanism has been suggested for the vulcanization of plastic chloroprene polymer (*3*), although little evidence exists to support such a process.

The existing evidence points almost entirely to the absence of polymerization during vulcanization. Spence and Scott (*12*) have presented evidence based on iodine absorption to show that no decrease in unsaturation occurs which cannot be directly accounted for by combination of sulfur. Fisher and Gray (*6*) have studied by the same method rubber vulcanized with nitro bodies or benzoyl peroxide. The authors conclude that any change in unsaturation was less than one per cent. The ability of rubber to combine with 32 per cent of sulfur without the evolution of more than small quantities of hydrogen sulfide is a further indication that little disappearance of unsaturation has taken place because of polymerization.

It should be possible to determine the extent of polymeri-

zation by following the change in density. During the polymerization of isoprene the specific gravity changes from 0.68 to approximately 0.90, or by a value of 0.22 with a loss of half of the double bonds (*4*). If loss of the remaining unsaturation should cause an increase in specific gravity of only 0.20, it should be possible by measuring within two units of the third decimal place to determine a loss of one per cent of the double bonds. Measurements have been recorded which indicate changes in density (*2*, *5*, *9*, *10*), but data are not available to separate the changes due to various existing factors.



The most efficient type of vulcanization is accompanied by combination of sulfur. The creation of the resulting organic sulfur compound will cause a change in density which will be measured along with any change in density caused by loss of unsaturation, and a suitable correction must be made. To do this, advantage may be taken of the fact that, by choice of vulcanizing conditions, greatly different states of vulcanization, as measured by modulus or tensile strength, may be obtained with the same amount of combined sulfur. If vulcanization is accompanied by a change in the state of polymerization, then changes in density should be influenced by both the amount of combined sulfur and change in physical properties, while the absence of polymeric change would be indicated by a linear relationship between combined sulfur and specific gravity, regardless of the physical properties of the rubber.

Experimental Procedure

The following compounding practice was adopted:

A quantity of pale crepe rubber was acetone-extracted and blended. The acetone extraction removed considerable resinous material which otherwise would have been converted at least partially into an unextractable sulfur compound. Zinc propionate was used as the accelerator activator when required because of its solubility in rubber and ease of extraction. The rubber was vulcanized between sheets of aluminum foil which were not re-

moved until just previous to making physical tests in order to protect the rubber from surface contamination and oxidation. Small samples of each cure were wrapped separately in cloth and acetone-extracted for 8 days. The position of the samples in the extractor was frequently changed to insure uniform extraction.

Specific gravity was determined indirectly by means of a hydrometer of such construction that the fourth decimal place could be estimated. The samples after acetone extracting were dried at a pressure of about 3 mm. of mercury in a desiccator containing calcium chloride. They were protected from air at all times as much as possible because of the rapid absorption of oxygen which is accompanied by an increase in specific gravity of a magnitude sufficient to cause serious difficulty. After drying, a strip approximately 1 mm. square and 4 cm. long was cut from the rubber. This was dropped into an alcohol-water mixture which was held at a temperature within 0.1° C. and which contained a small amount of sodium butyl naphthalene sulfonate to promote wetting of the surface. The gravity of the liquid was adjusted approximately, and the vessel was connected to a vacuum line for 2 minutes. The final adjustment of the gravity of the liquid was then made, after which the test sample was cut into four pieces. In case all four pieces when returned to the liquid did not have the same gravity, it was taken as an indication of bubbles or foreign material being contained in the rubber, and the test was repeated.

TABLE I. COMPOSITION OF COMPOUNDS CONTAINING ZINC

	25-A	25-B	39-B
Extracted pale crepe rubber	100.0	100.0	100.0
Zinc propionate	4.0	4.0	4.0
Sulfur	6.0	6.0	6.0
Phenyl-β-naphthylamine	0.5	0.5	0.5
Piperidinium pentamethylene dithiocarbamate	1.0	0.0	0.0
Butyraldehyde butylamine	0.0	0.0	1.0
Vulcanization temp., ° C.	115	145	140

TABLE II. PROPERTIES OF COMPOUNDS CONTAINING ZINC

Vulcanization Time	Load At 500% elongation	Load At break	$d^{29.0}_{15.0}$	Combined Sulfur
Minutes	*Kg. per sq. cm.*			%
		COMPOUND 25-A		
3	30	144	0.9197	1.29
10	95	172	0.9285	2.50
30	109	109	0.9332	3.17
60	89	184	0.9350	3.34
120	65	158	0.9355	3.43
		COMPOUND 25-B		
60	...	21	0.9235	1.13
120	4	65	0.9295	2.05
180	6	93	0.9355	2.74
240	9	91	0.9428	3.71
		COMPOUND 39-B		
3	11	123	0.9160	0.80
5	23	204	0.9212	1.38
10	33	187	0.9260	2.30
20	35	171	0.9320	3.22
30	32	165	0.9373	4.00
60	21	185	0.9484	5.40

Rubber compounds containing zinc propionate even after long extraction still contained small amounts of zinc. The amount remaining, while enough to have a measurable effect upon the specific gravity of the rubber, was not determined because of the difficulty of sufficiently accurate determination and because of the uncertainty in regard to the propor-

tion existing as zinc sulfide or zinc propionate. The amount of zinc remaining appears to be greater when the rubber is vulcanized at a higher temperature, probably because of the production of zinc sulfide, and slow-curing compounds vulcanized at high temperature appear to have slightly greater specific gravity than more rapid-curing compounds. The amount of zinc present is also probably influenced by the difference in solubilizing action of the different accelerators employed, which assist in the extraction by the formation of a complex or salt with the zinc.

Rubber compounds containing zinc propionate and accelerated with piperidinium pentamethylene dithiocarbamate and with a butyraldehyde butylamine reaction product were compared with a compound containing no accelerator. A base stock was first mixed which contained all but the accelerator. This stock was then divided and accelerator added to two portions. The vulcanization time and temperature were adjusted to suit each compound. The composition of each stock is shown in Table I and the properties are shown in Table II.

No relationship is apparent between either combined sulfur or specific gravity and the state of vulcanization. While the compounds all include practically the same range of specific gravity and percentage of combined sulfur, more than a tenfold difference exists in the load-carrying capacity at 500 per cent elongation. Such results emphasize that the degree of vulcanization should be defined in physical rather than in chemical terms.

The relationship between combined sulfur and specific gravity is shown in Figure 1. These curves indicate that change in density is due to nothing other than combination of sulfur. Curve 25-A, which includes greatly different physical states of vulcanization, shows no irregularity that would indicate density changes corresponding to the different physical states of the rubber. The slightly higher specific gravity of the unaccelerated compound is probably due to a greater content of unextracted zinc.

A similar set of experiments was conducted with a stock containing no zinc. In this case the accelerator employed was sparteine which is probably the most active known organic accelerator in the absence of metallic salts. The composition of the compounds is given in Table III and the physical properties are shown in Table IV.

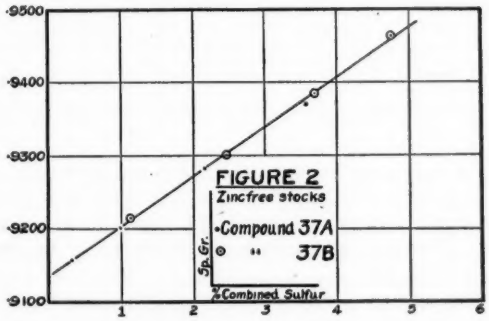
TABLE III. COMPOSITION OF COMPOUNDS CONTAINING NO ZINC

	37-A	37-B
Extracted pale crepe rubber	100	100
Sulfur	6	6
Sparteine	1	0
Vulcanization temp., ° C.	135	145

TABLE IV. PROPERTIES OF COMPOUNDS CONTAINING NO ZINC

VULCANIZATION TIME	LOAD At 800% elongation	LOAD At break	$d^{29.0}_{15.0}$ Unextracted	$d^{29.0}_{15.0}$ Extracted	COMBINED SULFUR
Minutes	*Kg. per sq. cm.*				%
		COMPOUND 37-A			
5	29	61	0.946	0.9157	0.32
10	37	94	0.947	0.9201	1.00
20	91	157	0.948	0.9283	2.18
30	178	204	0.951	0.9371	3.59
		COMPOUND 37-B			
60	17	64	0.946	0.9215	1.14
120	33	91	0.948	0.9301	2.48
180	51	134	0.950	0.9386	3.69
240	73	161	0.953	0.9465	4.76

The difference in the state of vulcanization between the two compounds in the absence of zinc is less than in the previous examples, but exactly the same relationships are shown. In this case the change in specific gravity before extraction is given and shows that a small decrease in volume takes place during vulcanization. The relationship between specific gravity after extraction and the amount of combined sulfur is shown in Figure 2 and indicates that the density change is due only to combination of sulfur.

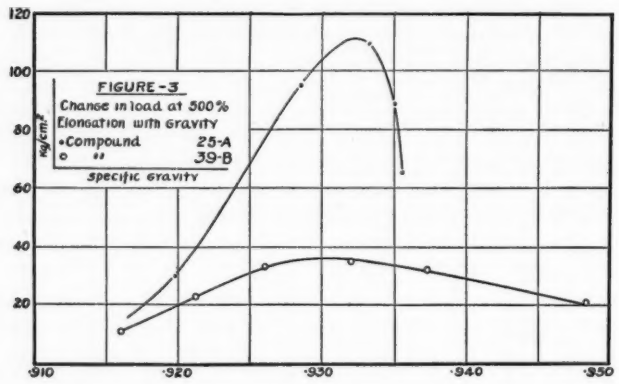


Rubber compounds when vulcanized for an extended time frequently begin to decline in modulus. This condition is commonly known as reversion and has been attributed to the dispersing or depolymerizing action of heat. Inspection of the data obtained with compounds 25-A and 39-B shows that the compounds continue to increase in density during cure, even during periods of reversion. This relationship which is shown in Figure 3 might be explained by some type of dispersion rather than by a depolymerization involving chemical valence which would in all probability cause a decrease in density.

It is possible that polymerization could take place beyond the limits which can be measured by the present method. The specific gravity determinations are probably correct, within 5 units of the fourth decimal place. If the writer's former assumption in regard to change in density with loss

of double bonds is correct, this accuracy would correspond to one double bond in 400 or to 400 original isoprene units, which would represent a molecular weight of 27,200 The present method would not detect the polymerization of larger units than this.

The present investigation has produced no direct evidence in regard to the nature of such dispersing or disaggregating actions as those proposed by Staudinger (*13*), Toyabe (*15*), Köln (*8*), and others, which precedes vulcanization. It should be noticed, however, that the most highly vulcanized compound reverts the most rapidly although vulcanized at



a much lower temperature. This would indicate a change in the vulcanized material as distinct from any change in unvulcanized rubber which might precede vulcanization. In the case of compound 25-A, reversion coincides with the practical disappearance of accelerator. This was shown by acetone extraction which removed an extract of feeble accelerating properties. The absence of accelerator was also indicated by diffusing in a fresh portion of accelerator, after which the normal rate of combination of sulfur was resumed when vulcanization was continued.

Conclusions

The present investigation shows that no direct relation exists between either combined sulfur or density and the degree of vulcanization. It is not probable that the various changes in physical properties of the rubber during vulcanization are due to changes in the polymeric state involving a change in primary valence forces. Neither is it apparent in what manner combination of sulfur has contributed directly to the change in physical properties of the rubber. It is probable that the change in physical state is due to a change in manner or degree of aggregation of the rubber molecules.

Literature Cited

(1) Axelrod, *Gummi-Ztg.*, **24**, 352 (1909).
(2) Blake, J. T., Ind. Eng. Chem., **22**, 741 (1930).
(3) Carothers, W. H., et al., *J. Am. Chem. Soc.*, 53, 4203 (1931).
(4) Conant and Tongberg, *Ibid.*, **52**, 1659 (1930).
(5) Ditmar and Preuse, *Rubber Age* (N. Y.), **27**, 595 (1930).
(6) Fisher and Gray, Ind. Eng. Chem., **20**, 294 (1928).
(7) Kirchhof, F., *Kolloid-Z.*, **14**, 43 (1914); **26**, 168 (1920).
(8) Köln, *Kautschuk*, **9**, 119 (1933).
(9) Kreps, *India Rubber J.*, **84**, 293 (1932).
(10) McPherson, Bur. Standards, *Sci. Paper* **560**, 385–98 (1928).
(11) Seidl, *Gummi-Ztg.*, **34**, 797 (1920).
(12) Spence and Scott, *Z. Chem. Ind. Kolloide*, 8, 308 (1911).
(13) Staudinger, H., *Kolloid-Z.*, **54**, 139 (1931).
(14) Stevens and Stevens, *J. Soc. Chem. Ind.*, **51**, 44T (1932).
(15) Toyabe, *Rubber Chem. Tech.*, **3**, 384 (1930).
(16) Whitby, G. S., *Inst. Rubber Ind. Trans.*, **6**, 61 (1930).
(17) Whitby and Simmons, Ind. Eng. Chem., **17**, 931 (1925).

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Measurement of Quality in Rubber Goods by Physical Tests

ARTHUR W. CARPENTER, B. F. Goodrich Company, Akron, Ohio

THE expression "measurement of quality" as applied to rubber goods seems at first thought to be quite definite; unfortunately, it conveys to different persons widely divergent ideas. Engineers in dealing with various materials often interpret the word "quality" as being synonymous with strength. Such usage is quite common in the rubber industry, and stocks possessing high tensile strength may be designated as high quality. A rubber compounder, on the other hand, may consider the quality of a rubber compound to be related to the percentage of pure rubber contained in the mixture. Thus, compounds having only small amounts of other materials added to the rubber would be considered high grade though they might be inferior in strength. Purchasers of rubber products have in the past shared both of these viewpoints, but today the more enlightened consumers understand the expression "high quality" to indicate the relative excellence of an article in performance of the intended service. This seems a more rational interpretation since, in the last analysis, satisfactory service is the prime objective and may or may not be affected by either great strength or high rubber content.

While quality of rubber articles in terms of strength or rubber content is comparatively easy to measure in the laboratory, and fairly satisfactory methods have long been more or less standardized, adequate laboratory evaluation of service behavior is quite another matter. Definition of quality on the basis of performance in service has therefore necessitated the development of new test methods. The older tests for particular properties which are still indispensable for the control of uniformity have been supplanted in product evaluation to a considerable degree by tests directly related to the service conditions. Just as the varieties of articles and types of service cover a tremendous field, so too these performance tests are exceedingly diverse and may be quite simple for some products or highly specialized and

complex for others. Some rubber articles are really structures requiring as complicated engineering as the building of a skyscraper, and the play of forces within them in service may be more complex and less capable of complete analysis than the stresses in the skyscraper. Testing such products involves more than merely the measurement of quality of the rubber compounds. Careful and complete analysis of both the structure and the service is necessary, after which development of a suitable test is worthy of the very best engineering thought.

Types of Physical Tests

The physical tests ordinarily made on rubber products may be considered as being in one of two classes, the first

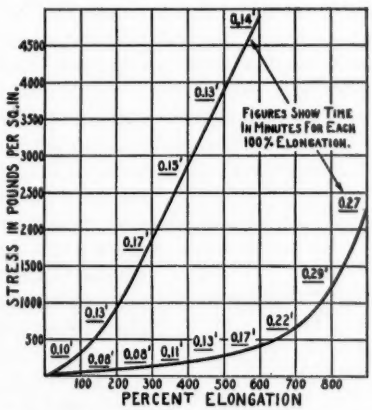

Figure 1. Rate of Stretching of Dumb-Bell Specimens between One-Inch Bench Marks

consisting of those which are designed to measure fundamental physical properties, and the second, those tests which aim to determine service value. Obviously no such classification can be rigid, for in many cases a certain particular physical property may govern the fitness of an article for service. The first class would include measurement of dimensions, of specific gravity, of tensile strength and ultimate elongation or the stress-strain relationship, of compressive strength and the relation between load and deflection, of hardness and resilience, of permanent set, color, dielectric strength, coefficient of friction, and the like. In the second class would be included tests for aging, adhesion, resistance to abrasive wear including tearing and cutting, fatigue tests of various kinds involving repeated applications of stress producing either extension, compression, or flexure, as well as a countless variety of service tests which represent attempts to imitate

the actual service under laboratory conditions in such a way that accelerated results may be secured.

The need for laboratory tests capable of giving information rapidly from which the behavior in service of rubber articles can be reliably predicted and the difficulties which have arisen in such use of present tests have been frequently emphasized. Bierer and Davis (*1*) pointed out the failure of tests of the first class to fulfill the requirements of purchase specifications and discussed the value of performance tests in this connection. They dealt particularly with the various tests for abrasive wear, accelerated aging tests, and a flexing test. While the weaknesses of these performance tests are fully appreciated, they are nevertheless considered to represent advance over the older tests. Dinsmore (*2*) has given a number of instructive examples showing the inadequacy and unreliability of the usual laboratory methods for the prediction of service performance. He selected stress-strain data, abrasion test results, and certain flexing tests, and referred to aging tests although various other tests might also, as he observed, have been included. He cited the variety of performance testing devices which have been developed in recent years as evidence that the need for better tests is well recognized and pointed out that such modifications as the work of Somerville and Russell (*6*) on testing rubber at higher temperatures and that of Somerville, Ball, and Edland (*5*) on autographic stress-strain curves of rubber at low elongations, are steps in the right direction. Dinsmore further suggests that, since rubber is partly plastic and partly elastic slow deformation emphasizes its plastic properties while fast deformation develops more elasticity. High temperatures appear to increase the plasticity effect at slow speed and elasticity effect at higher speeds. Degree of vulcanization is also an important factor. He considers it likely that this dual nature of rubber is important in many tests, mentioning particularly stress-strain, fatigue, adhesion, and possibly abrasion. Finally, he expresses another thought which seems especially

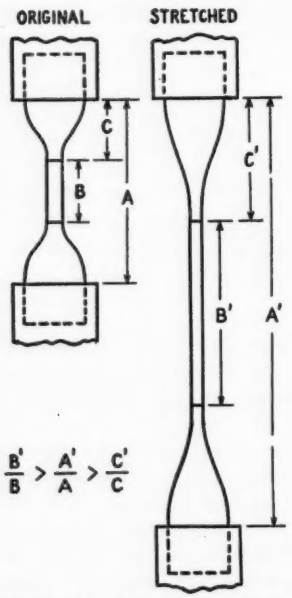

FIGURE 2. EFFECT OF DUMB-BELL ENDS ON RATE OF STRETCHING BETWEEN MARKS

worthy of elaboration and emphasis: "More effective laboratory methods may result from careful mechanical analysis of the behavior of rubber products in service. Rubber chemists have naturally failed to appreciate the full value of mechanical studies but they must turn to the physicist for aid in their difficulties. A sound theoretical basis may serve materially to shorten the tedious search for laboratory and service correlation. Certainly the haphazard development of new tests must lead but slowly to progress."

It would ordinarily be supposed that the oldest tests used for rubber products would have been thoroughly investigated and completely analyzed from a mechanical point of view. Two of these tests which were probably carried over from the field of the testing of metals are the measurement of tensile strength and elongation and the determination of hardness. Both of these have been used for more than a quarter of a century by rubber men and have been studied extensively. The lack of completeness of these studies can be illustrated by some data which were recently secured. In measuring tensile strength and elongation, it has usually been agreed that either a uniform rate of application of load or a uniform rate of stretching is desirable for producing duplicable test conditions. Since machines for applying load uniformly would be considerably more complicated than those designed for uniform rate of jaw separation, the latter have quite generally been used. How serious any departure from uniform loading or uniform stretching might be in its effect on the final results is irrelevant in connection with the present question of mechanical analysis. Presumably, the tensile testing machines were intended to give uniform stretching since care has been taken in all specifications to require a uniform and standard rate of jaw separation. A study was made of the actual rate of the stretching of dumb-bell rubber samples between one-inch bench marks when tested in a type

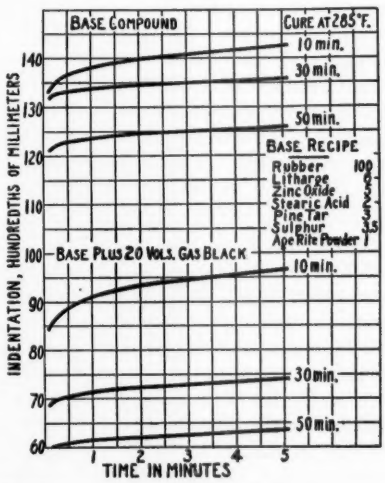

FIGURE 3. EFFECT OF DURATION OF LOADING ON INDENTATION HARDNESS

(Pusey and Jones plastometer)

L-6 Scott tester. The machine was first carefully checked under load to be certain that the speed of lower jaw travel was uniform and independent of load. Stop-watch measurements of the time required for each 100 per cent elongation between the marks were made by two observers. The data are shown in Figure 1. The time for 100 per cent increments of extension between the bench marks is not uniform for a high-rubber stock having low modulus but increases from 0.08 minute at the start to a maximum of 0.29 minute. In the case of a high-modulus tread stock, the rate is very much more uniform. Evidently, then, the rate of elongation measured with bench marks and dumb-bell samples is influenced by the modulus of the sample. It is believed that the explanation rests in the stretching of the enlarged ends outside of the bench marks. When under sufficient stress these also yield, relieving the elongation of the portion between the marks. This effect is illustrated in Figure 2. While A increases to A', B and C do not increase to B' and C' in the same ratio, and the extension of C lowers the rate of extension of B.

A simple study of two instruments for measuring indentation hardness again illustrates the lack of complete analysis in the case of even this very old test. It also adds weight to Dinsmore's view of the importance of the dual plastic and elastic nature of vulcanized rubber. Differences in relative hardness values were noted in an investigation of certain compounds when using the Shore durometer and the A. S. T. M. hardness tester. The results with three of these compounds are shown in Table I. It must be remembered that, in the A. S. T. M. instrument, the indenting point operates under a dead-weight load, and readings are not taken until after at least 30 seconds of weight application. The durometer, on the other hand, is a spring instrument, and the quickest possible and highest reading is taken. The scales of the two instruments read in reverse; that is, the higher durometer readings represent harder stock while the higher readings of the A. S. T. M. instrument show softer stock. Thus, the results on the 30-minute cures using the A. S. T. M. test show stocks A and B to be of substantially the same hardness while stock C appears decidedly more hard. The durometer test, however, indicates that stocks B and C are of the same hardness and that both are harder than stock A. If we bear in mind that undercures, such as the 30-minute cure of stock B, should be more plastic than correct or overcures, such as those of stocks C and A, the differences with the two instruments can be readily explained on the basis of plastic flow of stock B which affects the A. S. T. M. measurement but not the durometer reading. This is confirmed by the readings at the best cures. A further check (*8*) was made using a high-rubber stock and a 20-volume gas black compound in three cures, measuring hardness with a Pusey and Jones plastometer which is also a dead-weight indentation instrument. Read-

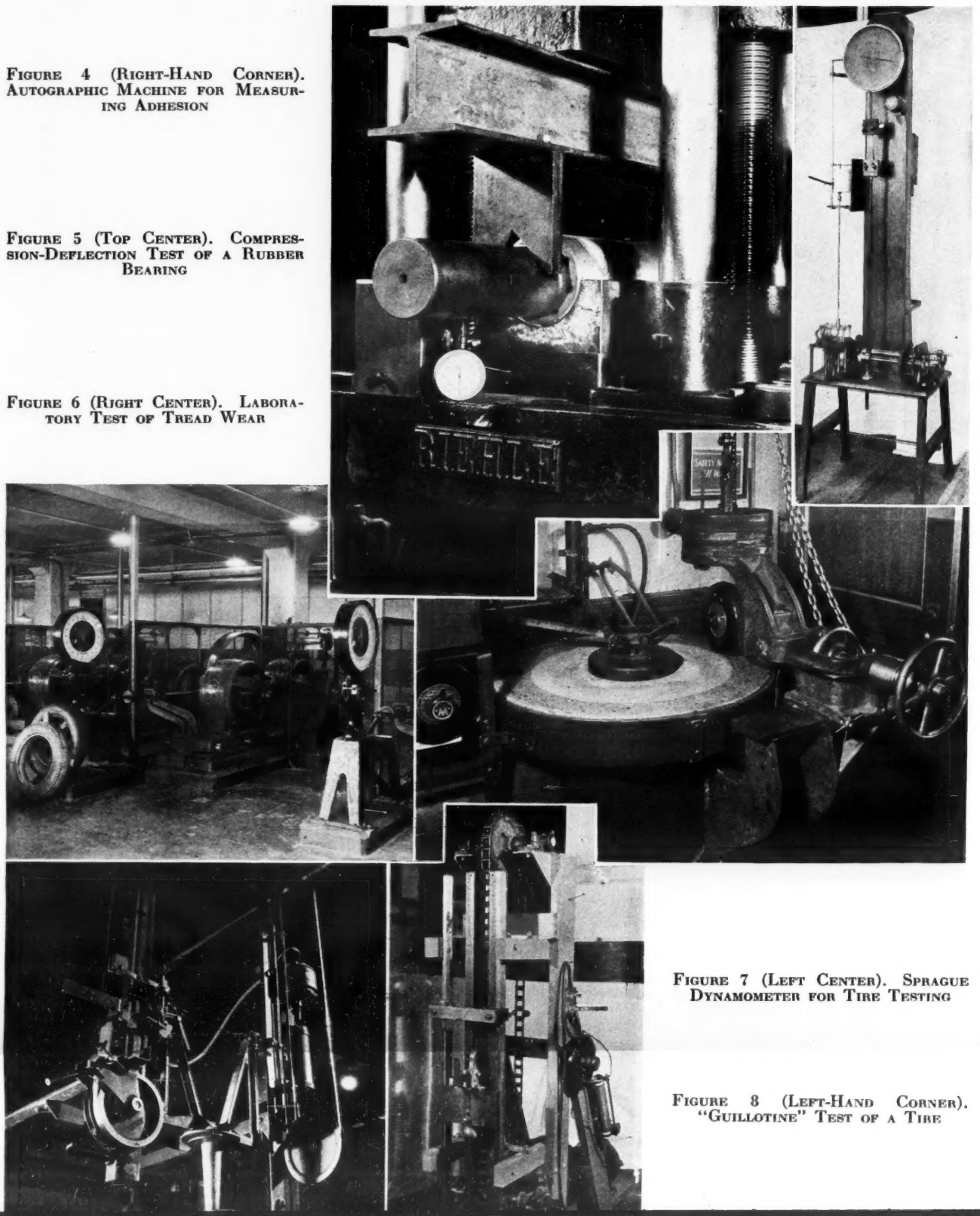

FIGURE 4 (RIGHT-HAND CORNER). AUTOGRAPHIC MACHINE FOR MEASURING ADHESION

FIGURE 5 (TOP CENTER). COMPRESSION-DEFLECTION TEST OF A RUBBER BEARING

FIGURE 6 (RIGHT CENTER). LABORATORY TEST OF TREAD WEAR

FIGURE 7 (LEFT CENTER). SPRAGUE DYNAMOMETER FOR TIRE TESTING

FIGURE 8 (LEFT-HAND CORNER). "GUILLOTINE" TEST OF A TIRE

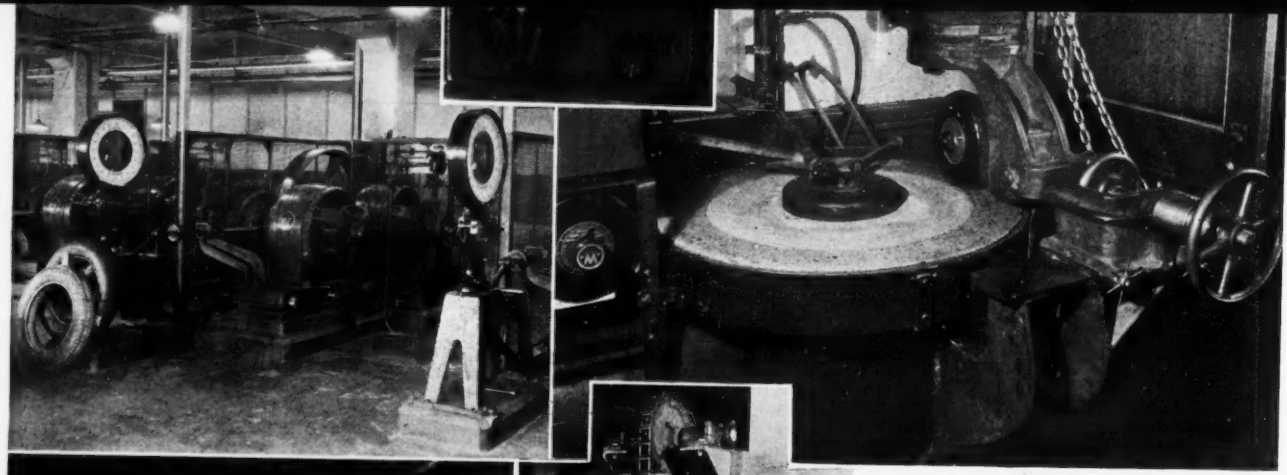

FIGURE 7 (LEFT CENTER). SPRAGUE DYNAMOMETER FOR TIRE TESTING

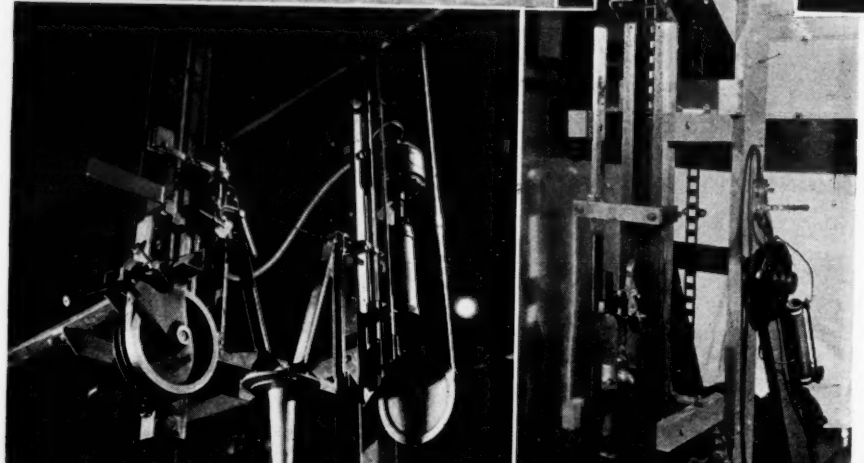

FIGURE 8 (LEFT-HAND CORNER). "GUILLOTINE" TEST OF A TIRE

"Guillotine" Test of a Tire

Figure 9 (Bottom Center). Drop Hammer for Impact Tests

ings were taken over a somewhat extended period. The results are shown in Figure 3. The curves for the undercured stocks (10 minutes at 285° F.) show plainly the effect of plastic flow, some of which persists even in the overcures (50 minutes at 285° F.) as shown by the slopes of these curves. Hardness of vulcanized rubber compounds thus appears to consist of two parts, one of which is due to resistance to resilient deformation and the other to resistance to plastic deformation. Some methods of measurement include both in the indentation hardness result, and other methods show only the resilient hardness depending on the duration of the application of the load.

The significance of this kind of analysis in making possible better correlation with service has been intentionally omitted from the discussion because much more work will be necessary before it can be fully evaluated. Surely, however, such analysis cannot help but give us better appreciation of the value of the tests which are made and a more accurate understanding of how to use the test data. We must not fail to realize the indirect nature of all laboratory tests nor should we underestimate their value for comparative purposes, even though direct correlation with service is not always clear. Certainly, direct interpretation in terms of service value is not possible for tests such as determinations of stress-strain relationships, permanent set, and adhesion, except in some special instances. Yet, what rubber technologist would be willing to have such useful tools taken from him and would be content to rely on imitations of service and on simple hand tests alone? Service evaluation or prediction represents a judgment on the part of the technologist, and all of the information possible, comparative and indirect, as well as direct data, must be assembled if the final estimate is to be a good one.

Difficulties in Correlating Laboratory and Service Results

The difficulties which are experienced in correlating laboratory test results with service performance must be attributed to one or both of two causes. Either the tests themselves are improperly designed or the results secured from the tests are not correctly interpreted. Improper design is a frequent consequence of hasty, unsound analysis of the service which fails to give full knowledge and appreciation of all the conditions and forces that are involved. A fundamental requirement of good testing is that the service to be measured shall be first completely and accurately defined before attempting the design of a test. A good example of the lack of such definition is found in the case of abrasive wear, particularly as applied to tread wear of tires. The various conditions and forces involved are so numerous and complex that we frankly admit our shortcomings in respect to their analysis. Yet we attempt to design laboratory abrasion tests and we carry on

TABLE I. COMPARISON OF A. S. T. M. AND DUROMETER HARDNESS

STOCK	BEST CURE AT 280° F.	SAMPLES AT BEST CURE					CURE, 30 MIN. AT 280° F.		
		Tensile strength	Ultimate elongation	Modulus at 300% elongation	A. S. T. M. hardness	Durometer hardness	A. S. T. M. hardness	Durometer hardness	Permanent set, stretched[a]
	Min.	*Lb./sq. in.*	*%*	*Lb./sq. in.*					
A[b]	15	2650	660	600	125	39	78	50	34
B[c]	45	1570	400	950	69	59	75	57	60
C[d]	30	1070	425	650	69	56	65	58	25

[a] 80 per cent of ultimate.
[b] Stock A (parts by weight): rubber, 36.5; inner tube reclaim, 36.5; zinc oxide, 6.5; mineral rubber, 11.0; palm oil, 1.3; sulfur, 3.2; accelerator, 5.0; total, 100.0.
[c] Stock B: 100 parts A + 82.5 Georgia clay.
[d] Stock C: 100 parts A + 82.5 Missouri clay.

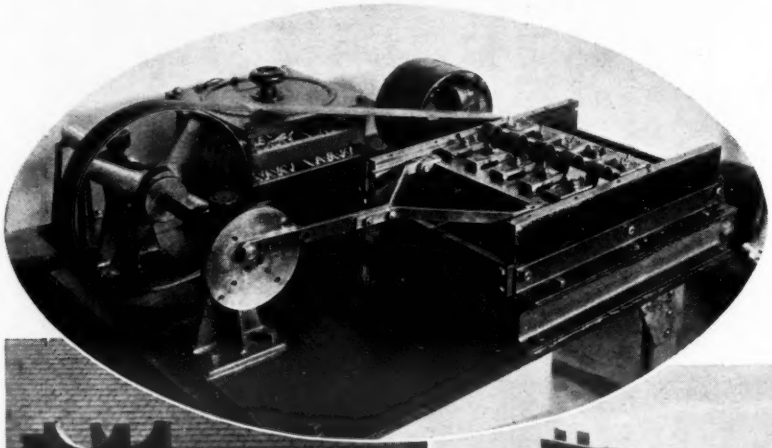

FIGURE 10 (LEFT). FATIGUE TESTING IN FLEXURE

FIGURE 11 (BELOW). FLEXING TEST FOR SOLING

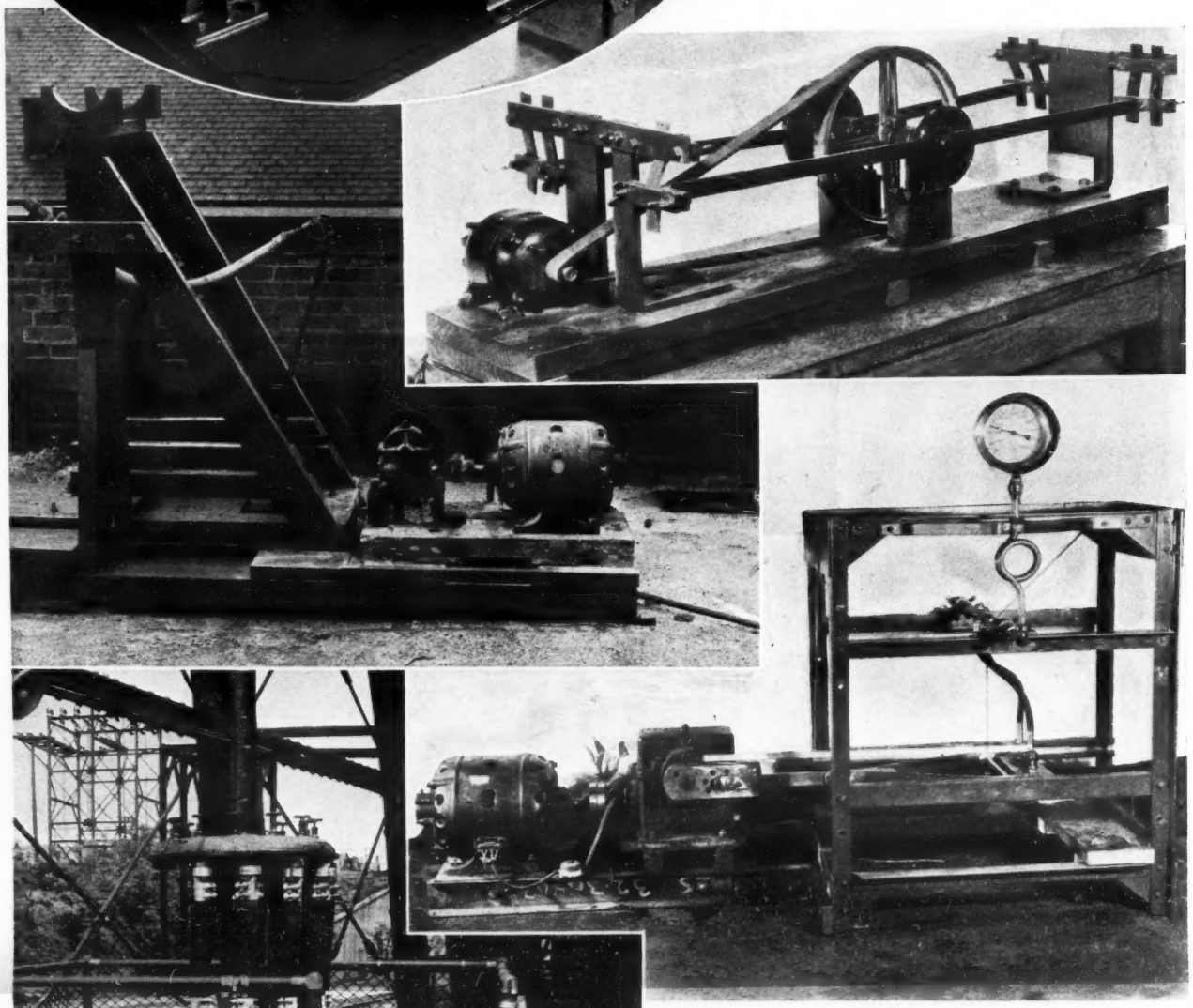

FIGURE 12 (LEFT CENTER). FLEXING TEST OF GASOLINE HOSE WHILE CONTAINING LIQUID

FIGURE 13 (ABOVE). FLEXING TEST OF GREASE-GUN HOSE UNDER 2500 POUNDS PER SQUARE INCH GREASE

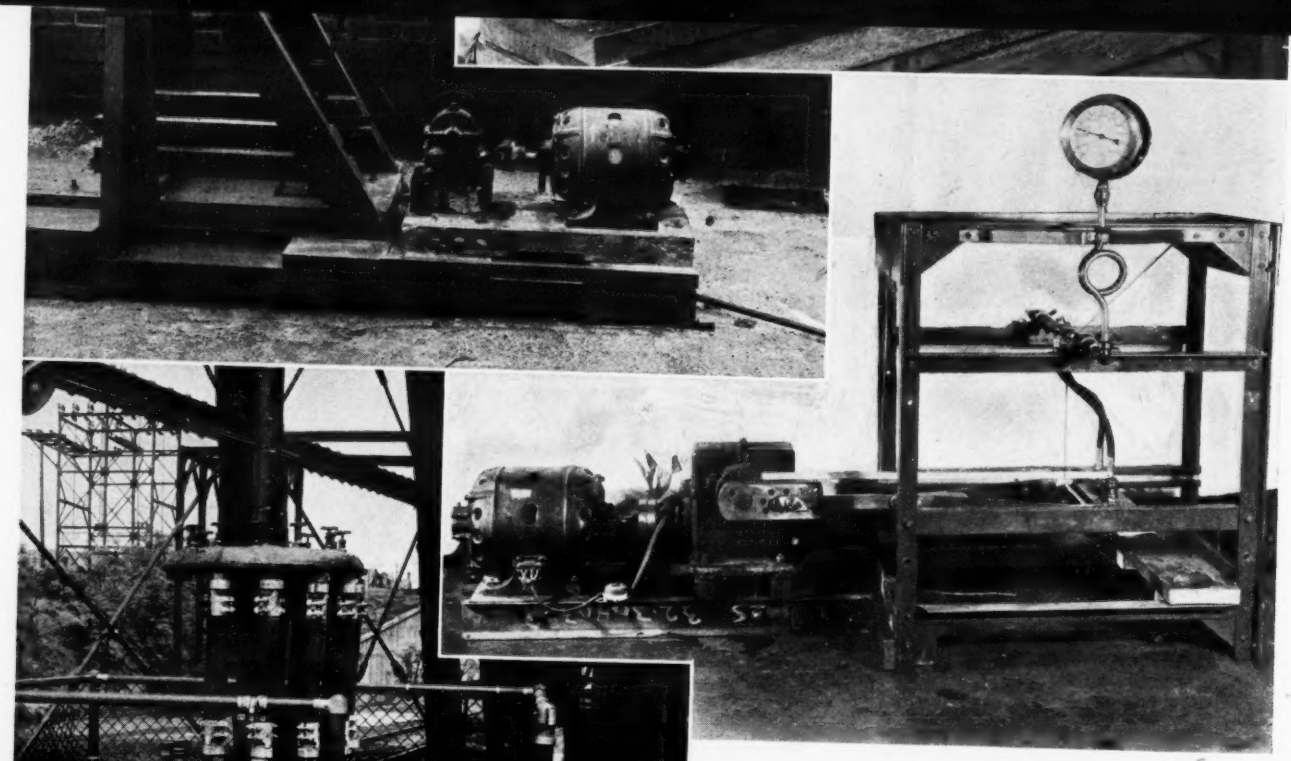

FIGURE 12 (LEFT CENTER). FLEXING TEST OF GASOLINE HOSE WHILE CONTAINING LIQUID

FIGURE 13 (ABOVE). FLEXING TEST OF GREASE-GUN HOSE UNDER 2500 POUNDS PER SQUARE INCH GREASE PRESSURE

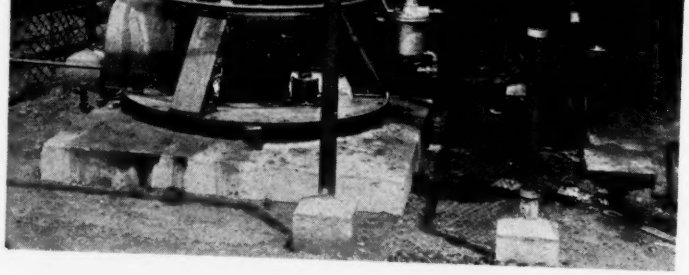

FIGURE 13 (ABOVE). FLEXING TEST OF GREASE-GUN HOSE UNDER 2500 POUNDS PER SQUARE INCH GREASE PRESSURE

FIGURE 14 (LEFT). PERFORMANCE TESTING OF STEAM-HOSE TORSIONAL FLEXING UNDER 250 POUNDS PER SQUARE INCH STEAM PRESSURE

extensive road testing at enormous expense without really knowing what it is we are trying to measure. Possibly more time and money spent in determining just what road wear consists of and in establishing the relative importance of the various service factors might pay more dividends in the end than all of these expensive test programs. Proof of the serious inadequacy of present analyses of road wear factors is evidenced by the difficulties which different tire manufacturers have in checking one another's road tests, and by the fact that each manufacturer has elaborate sets of road test data which show that his tires are the best of all competitive brands. It is worthy of note that laboratory abrasion tests do correlate fairly well with service wear when the latter is simple enough to be readily analyzed or capable of being closely duplicated under laboratory conditions.

Improper design of laboratory tests may result also from failure to carry over into the test apparatus a proper balance of the conditions and forces known to exist in the service. This is often caused by the necessity of accelerating the investigation. Performance tests would fall short of their purpose if they required as long a time as the service life of the article. The acceleration of failure is secured usually in one or more of the following ways: (1) by increasing the severity and intensity of forces on the sample (higher pressures or loads, harsher abrasive surfaces, etc.); (2) by increasing the temperature; and (3) by increasing speeds. Through emphasizing certain of these individual factors, the normal balance of service conditions may be upset, both directly and, as is often not realized, indirectly, since change in one condition may cause resultant changes in others. Obviously, without such emphasis the test would not be accelerated. If the emphasized conditions are those which are principally responsible for the ultimate failure of the article and if the other factors which are involved are not important in contributing to the cause of failure even though they may be indirectly affected, reasonable success may be anticipated with respect to correlation of such tests with service. On the other hand, when the balance of the service factors is seriously disturbed in the test conditions, it is unlikely that good correlation can be obtained. The only alternative which remains then is to analyze the service completely and emphasize all factors in the same proportion.

In regard to interpretation of laboratory tests, it is not infrequent that attempts are made to apply test data to services that involve differences in conditions which are significant but not fully appreciated. Here, again, the solution of the difficulties which arise must reside in more careful analysis of both the test and the service. It is also quite usual to encounter lack of understanding of the limits in precision of engineering data secured by test. Almost

any of the performance tests serves to eliminate products which are radically unfit for the intended services. It is only when finer distinctions are involved that serious reversals are encountered. For instance, several of the better abrasion resistance tests will distinguish between first grade and second grade treads when the actual service differences in the treads are fairly wide and when the treads have similar degrees of hardness. It is only when close comparisons between treads of dissimilar hardness characteristics are required that serious reversals occur. While such accurate measurement and correlation are extremely desirable and may some day be possible when we have learned to analyze all of the conditions closely enough, it must be admitted that as yet we are somewhat in the position of trying to weigh a dust particle with ordinary counter scales.

Laboratory Tests

Some pictures of laboratory testing which follow are shown, not with any idea that they may serve as shining examples of perfect mechanical analysis or as the last word in quality measurement, but merely that they may be suggestive as to the modern trend of test development and may illustrate the simplicity of the mechanical movements at present utilized in developing performance tests. As has already been suggested, the details of such tests are extremely varied but the fundamental mechanical principles are not nearly so diverse as appears at first glance. Figure 4 shows a machine test for adhesion or "friction pull." The specimen in this case is a strip of transmission belting one inch in width. This test involves simply the measurement, by means of a pendulum dynamometer head, of the force required to separate plies of the specimen under standardized conditions. As has been frequently pointed out in the literature, the correlation of such tests as this with service performance is extremely unsatisfactory. Figure 5, however, shows a test in which the service correlation is very positive. In this case the deflection of a rubber bearing is being measured under various compressive loads applied to a shaft by means of a universal testing machine.

As has been suggested, performance tests which appear to be very good imitations of service conditions often fail to give satisfactory service correlation, probably because of failure to include in the test the essential characteristics of the actual service. Figure 6 illustrates such a case. This machine was designed to test tread wear, using as test specimen a small pneumatic tire which is run on a rotating track made of standard road concrete. The test is of the angle-slip type and provision is made for control of the angle. The speed can be varied as well as the dead-weight load supported by the tire. The road wheel is the driven member and in turn, through contact, rotates the tire wheel which is mounted

FIGURE 15 (RIGHT). COMPARATIVE PERFORMANCE TEST OF PNEUMATIC TOOL HOSE

FIGURE 16 (BELOW). PERFORMANCE TEST OF STEAM VALVE DISKS

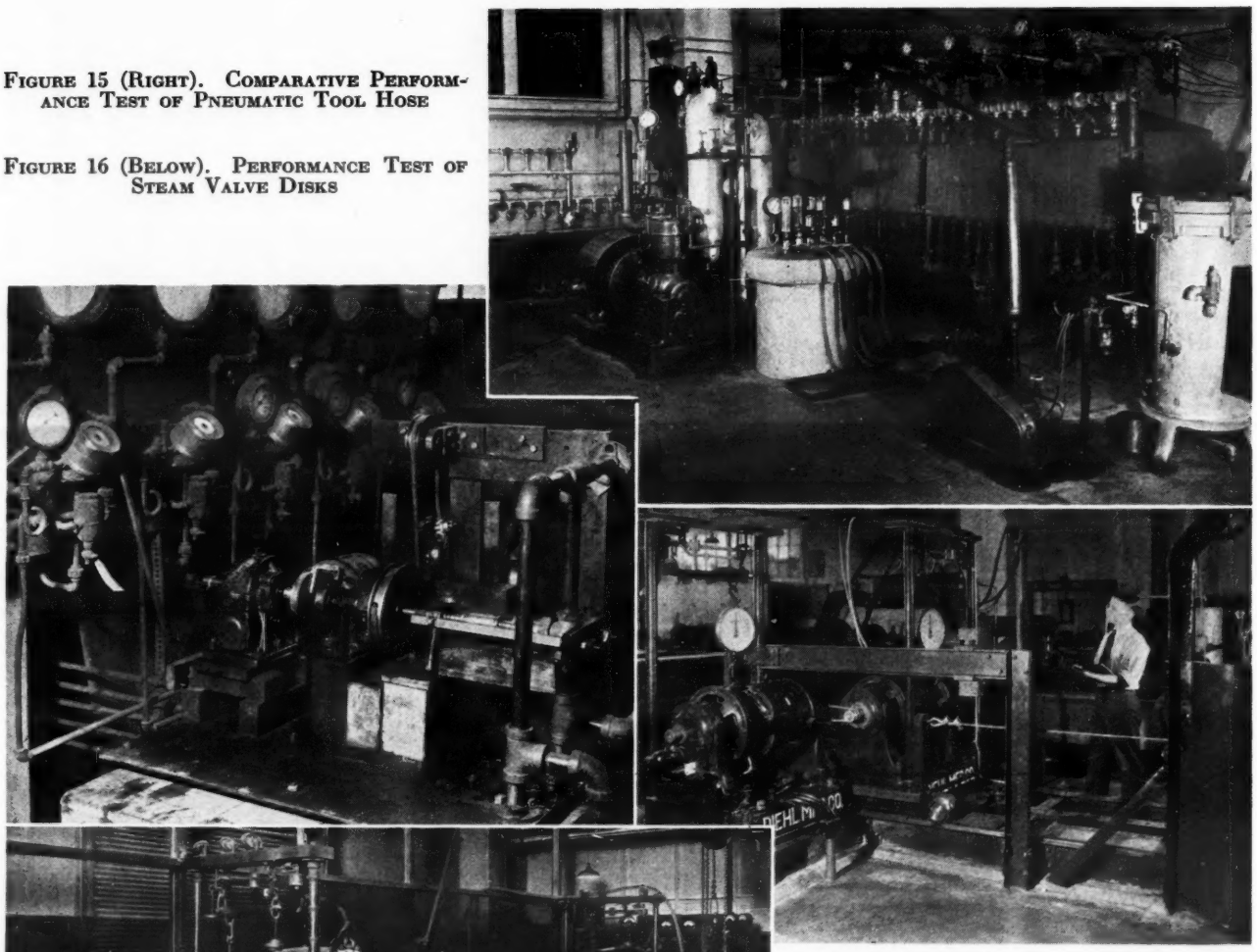

FIGURE 17 (ABOVE). HIGH-SPEED, 25-HORSEPOWER DYNAMOMETER FOR TESTING SMALL BELTS

FIGURE 18 (LEFT). ONE-HUNDRED-HORSEPOWER SPRAGUE DYNAMOMETER FOR TESTING POWER-TRANSMISSION BELTING

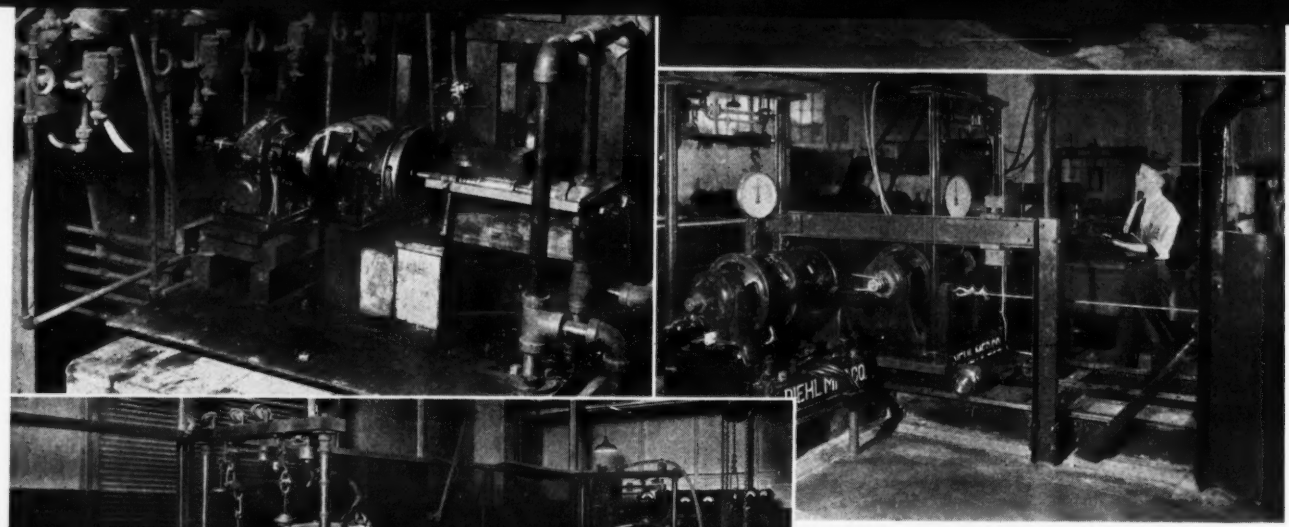

FIGURE 17 (ABOVE). HIGH-SPEED, 25-HORSEPOWER DYNAMOMETER FOR TESTING SMALL BELTS

FIGURE 18 (LEFT). ONE-HUNDRED-HORSEPOWER SPRAGUE DYNAMOMETER FOR TESTING POWER-TRANSMISSION BELTING

as an idler on ball bearings. The amount of tread wear is measured by accurately calipering the depth of the nonskid grooves. For a time it appeared that this test would correlate very reliably with actual road service, but, as often happens, it was necessary only to continue testing on a sufficient number of tires to encounter serious reversals.

In Figure 7 is shown a view of tire testing on Sprague dynamometers. In such tests a generator is driven by a motor through controlled contact of tire and road wheel. The actual horsepower expended on the road wheel is measured by weighing the generator torque and measuring the speed, using the Prony brake formula for the calculation. These tests have been quite reliably correlated with actual service for the evaluation of tire carcass performance. Figure 8 shows a rather obvious but useful impact test known as the "guillotine test." This has given valuable information concerning the ability of tires to withstand service conditions. In this case the impact member is dropped between guides from controlled heights in an elevator shaft, striking a blow of known force on an inflated full-sized tire, properly mounted.

Another device for impact testing, as shown in Figure 9, has been successfully used for the testing of rubber-covered metal plates, such as are used in lining chutes, grinding mills, etc. In this device a chain elevator raises a 50-pound weight carrying a hemispherical impact surface to a predetermined height at which the weight is tripped from the elevator. The heavy body falling freely between nearly frictionless guides strikes a blow of known force on the specimen placed below on a suitable solid support. A very interesting result was observed with this apparatus while testing sheets of rubber which had been bonded firmly to metal backing (*3*). Certain specimens, when tested dry, required approximately one hundred blows before complete failure, which was taken as the number of impacts necessary to cause the rubber to tear apart sufficiently to expose the metal base. In appearance the failed sample showed a very roughened surface over a circular area of diameter about equal to that of the impact ball. At the center of this area a circular hole of small diameter extended down through the rubber to the metal. When the experiment was repeated, with the difference that the surface of the rubber was kept wet with water, failure took place after three or four blows. Irregular radial cracks extended from the center of percussion outward, and there was no appreciable roughening of the surface. Apparently the water acted as a lubricant, concentrating the full force of the blow at the center of percussion rather than permitting the energy of the blow to be dissipated through a larger volume of rubber by means of friction.

Figures 10 to 14 show applications of flexing tests to various rubber products. Such tests can seldom be corre-

lated directly with service performance, but they are extremely useful for comparative purposes. The machine illustrated in Figure 10 is used with rubber strips or dumbbell specimens and is similar to the DeMattia flexing machine (*4*). A crosshead is driven by an eccentric at controlled variable speed. By using suitable settings of the clamps, it is possible to flex the rubber samples in bending only, as shown, or in extension. In either case the first sign of failure will be the development of small cracks which finally lead to a complete rupture of the specimen. Figure 11 shows a bending fatigue test on soling stock. This differs from the previous test in that the specimens are under slight tension produced by the weight of the driving arms which are supported by the specimens. In Figure 12 the performance relationship is more clearly defined, for in this case a specimen of gasoline hose full of the liquid is bent back and forth until the tube fails and the gasoline penetrates into the body of the hose. Figure 13 shows specimens of grease-gun hose filled with grease under high pressure, which are flexed with a reciprocating motion until failure and consequent release of the pressure take place. Figure 14 shows a recent performance test for steam hose. In this case the lower platform moves with an eccentric motion, causing the lower end of the hose specimen to be rotated in a circle about 4 inches in diameter. During test the hose is subjected to internal steam pressure of 250 pounds per square inch and external action of the weather. It is thus quite typically a performance test imitating actual service conditions as encountered by railway steam hose.

Another performance test, in which a rather elaborate attempt is made to duplicate on a laboratory scale, a complicated set of service conditions, is shown in Figure 15. In this case, service life of four samples of pneumatic tool hose is being compared. The apparatus consists of an air compressor which discharges into a receiver through equipment arranged to give constant temperature and pressure in the receiver. The compressed air from the receiver flows through the hose specimens after having received a known addition of lubricating oil at the receiver outlet. The compressed air is released from the hose through a valve mechanism which duplicates the impulse action of a pneumatic hammer. The test may be accelerated by raising the temperature and pressure of the compressed air. Figure 15 also shows a steam rack and a digester which are used for heat deterioration tests of hose specimens. In Figure 16 equipment for testing steam valve disks is shown. A valve installed in a high-pressure steam line contains the disk under test, and mechanical arrangements are provided whereby the valve is opened by a motor which raises a weight at the same time. The mechanism then trips and the falling weight closes the valve, assuring duplicate force conditions at each closure.

Figures 17 and 18 show dynamometer equipment for testing belts. Both of these sets are so arranged that very complete information can be secured. In each case one dynamo is mounted on a track which permits control and measurement of the total tension on the test belt. In each set both dynamos are cradled and equipped for torque and speed measurement so that the actual pulley horsepowers can be calculated excluding the dynamo losses. In each case one dynamo operated as a motor drives the other dynamo as a generator through the belt. Knowing the pulley horsepower in each case, the power transmission efficiency is determined. The effective power load can be regulated by means of adjusting known resistances in the generator discharge circuit. With a given total tension on the belt, it is possible to use so much resistance that slippage of the belt occurs as would be evidenced by the readings of the revolution counters on the units. The set shown in Figure 17 was recently designed for testing small V-belts at high speeds. It is capable of being operated continuously at speeds up to 5000 r. p. m. with power loads of 25 horsepower. The set shown in Figure 18, similar to that previously described by Sturtevant (*7*), is capable of handling 100 horsepower at speeds up to 1800 r. p. m. It is suitable for use with full-size power-transmission belting of either flat or V-type.

It is hoped that this discussion and the illustrations may serve to stimulate ideas and work which will lead to progress in development of well-designed laboratory performance tests and their correlation with service.

Literature Cited

(1) Bierer, J. M., and Davis, C. C., *Trans. Inst. Rubber Ind.*, 3, 151–78 (1927).
(2) Dinsmore, R. P., *Ibid.*, 7, 407–14 (1932).
(3) Sargisson, Z. E., B. F. Goodrich Co., unpublished work.
(4) Somerville, A. A., *Trans. Inst. Rubber Ind.*, 6, 141 (1930).
(5) Somerville, A. A., Ball, J. M., and Edland, L. A., Ind. Eng. Chem., Anal. Ed., 2, 289 (1930).
(6) Somerville, A. A., and Russell, W. F., Ind. Eng. Chem., 25, 1096 (1933).
(7) Sturtevant, W. L., *India Rubber World*, 83, 68 (Dec., 1930).
(8) Tronson, J. L., B. F. Goodrich Co., unpublished work.

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Alanine in Rubber Latex

J. McGavack and J. S. Rumbold, United States Rubber Company, Passaic, N. J.

INDIRECT evidence of the presence of amino acids in ordinary ammonia-preserved latex was obtained from electrometric titration work with the glass electrode, the application of which to latex was described in a previous article (*2*).

A small sample of alanine has now been isolated and identified, and indication of the presence of phenylalanine has also been obtained; however, owing to the small amount of material, its identification could not be established.

It is believed that this is the first amino acid to be isolated from latex in the pure state and positively identified; the fact that it has not been detected before may be due to the small amount usually present and to the great solubility of the substance. The only reference found in the literature relating to the presence of an amino acid in rubber is the article by Whitby, Dolid, and Yorston (*3*). These workers obtained a small amount of *d*-valine from the acetone extract of pale crepe.

Glycine, proline, and leucine are apparently either absent or present in relatively small amounts. If the amino acids are derived from decomposition of proteins, the absence of glycine is rather remarkable since most proteins with a high alanine content—for example, silk fibroin—also contain this amino acid.

Allowing for unavoidable loss, the amount of alanine isolated in the pure state is, as was expected, not enough to account for slope at the half-way point of the latex potentiometric titration curve. Although reasonable precautions were taken to avoid loss, no effort was made to obtain quantitative data, but from the amount of pure alanine obtained (about 1.5 grams from 7 liters of latex serum) it is thought that the alanine content of the original latex could not have been more than about 0.03 per cent. A solution of alanine of this strength is about 0.003 *N*. It appears likely that there must be several other amino acids of which the dibasic glutamic acid, commonly occurring in plant proteins, may be one.

Method of Extraction

The method employed for the extraction of the amino acids was the classical one of Emil Fischer. Chiefly on account of the presence of quebrachitol and a large amount of soluble impurities, attempts to obtain an amino acid by the action of solvents on the dried serum always failed. The only substance obtained by this method was quebrachitol, which crystallized readily from alcohol after repeatedly boiling the solution with animal charcoal. The following procedure was successful in isolating an amino acid:

About 7 liters of latex serum, prepared by creaming some ammonia latex with ammonium alginate, were stirred in a current of air until there was no odor of ammonia. The object of this preliminary treatment was to reduce the amount of ammonium chloride which would be formed on addition of hydrochloric acid, but it was probably unnecessary.

The residual rubber, etc., was coagulated by a little dilute hydrochloric acid and removed by filtration. The resulting clear serum was neutralized and evaporated to a dark brown viscous sirup, 200 cc. of absolute alcohol were added, and the amino acids were esterified by saturating the alcohol with dry hydrochloric acid gas.

The alcohol was evaporated off *in vacuo* below 50° C., and the sirup was again treated with alcohol and hydrochloric acid. The nearly black viscous residue obtained by evaporation of the alcohol was dissolved in one-third to one-half the volume of water and poured into a 2-liter flask.

Seven hundred cubic centimeters of ether were added, and the mixture was cooled in a freezing mixture. Ice-cold 30 per cent sodium hydroxide was added in small quantities at a time until the hydrochloric acid was neutralized, and then solid potassium carbonate; the flask was continually shaken in the freezing mixture. The ether was poured off and replenished by a fresh quantity. Solid potassium carbonate and sodium hydroxide solution were added gradually to form finally a thick mass which was shaken out repeatedly with 500-cc. lots of ether until the ether separated in a nearly colorless state. About 4 quarts (4.6 liters) of ether were required for the extraction.

The ethereal extracts were dried by shaking for about 10 minutes with potassium carbonate, and were then combined and left overnight with anhydrous sodium sulfate.

The ether was evaporated in small quantities at a time by passing a current of dry air over the solution at the ordinary temperature. A light brown oil was left which was fractionally distilled *in vacuo*, using a Cenco vacuum pump, the receiver being cooled with solid carbon dioxide. The following fractions were collected:

Fraction	Temp.	Pressure	Weight
	° C	*Mm.*	*Grams*
I	20	11.0	41.8
II	20- 60	11.0	12.1
III	60–100	5.0	2.0
Residue	....	..	2.0

Isolation of *d*-Alanine

The first fraction consisted almost entirely, and the second very largely, of alcohol which had been dissolved by

the ether, since the viscous nature of the original sirup prevented complete removal of the alcohol used in the esterification process.

Fractions II and III were colorless oily liquids, which, when added to water, dissolved completely to give strongly alkaline solutions. (The amino acid esters are strong bases owing to the blocking of the carboxyl group by the ethyl radical.) The solutions were boiled with water under a reflux condenser until the alkaline reaction disappeared and were then evaporated to dryness in weighed flasks.

The total weight of residue from fractions I and II was only about 2.5 grams. The constituents might be glycine, alanine, leucine, and proline.

The residues were combined and extracted several times with boiling absolute alcohol, and the alcoholic extracts were evaporated to dryness. This treatment removed some of the coloring matter but apparently very little else, and it may therefore be concluded that proline, which is appreciably soluble in alcohol, was either absent or present only in very small amount.

The amino acids insoluble in alcohol were dissolved in water and completely decolorized by boiling the solution with animal charcoal; the solution was then slowly evaporated on a water bath. However, it had to be taken down to very small bulk before any crystals appeared. They were filtered off, alcohol was added to the filtrate until the mixture became slightly turbid, and it was heated on the water bath for a few minutes and cooled in ice. A good crop of small colorless needles was obtained; they melted at 286° C. (uncorrected) and had a sweet taste (melting point of *d*-alanine, 297° C.).

Three recrystallizations from aqueous alcohol raised the melting point to 290° C. (corrected), and after seven recrystallizations the compound melted at 295° (corrected). Since the first crop of crystals apparently also consisted chiefly of the same substance, it was purified in the same way and combined with the rest.

The crystals melted in a capillary tube to a brown liquid, which decomposed with a rapid evolution of gas. A sample of *d*-alanine (melting point, 293° C.) had a melting point determined by the same thermometer of 294°.

Further characterization was obtained by a determination of the nitrogen content: found, 15.5 per cent; calculated (for alanine), 15.7.

The residue from fraction III was too small to be further examined.

Examination of Residue (Undistilled, Higher Boiling Esters)

The brown sticky substance left in the distilling flask was extracted with ether, and the ether was evaporated *in vacuo*. The resulting dark brown oil was mixed with about 5 volumes

of water; only a part dissolved, the rest remaining as a brown oil. This indicates that a considerable amount of the ether-soluble portion of the residue consisted of phenylalanine ester, which differs from the esters of aspartic acid, glutamic acid, and serine by being only slightly soluble in water.

The aqueous solution containing the insoluble oil was extracted with an equal volume of ether, and the ether extract was washed several times with water to remove traces of any of the other esters which might have been dissolved. The ether was removed, and the ester hydrolyzed by boiling with concentrated hydrochloric acid.

It gave a dark brown solution. Crystals could be seen on the side of the flask, and a brown insoluble substance was formed. The solution was boiled with animal charcoal, filtered, and evaporated to dryness. A crystalline substance was left, but it was too small to be identified.

Electrometric Titration of the Latex Amino Acid

By means of the titration curve we can determine the acidic dissociation constant and the combining weight of the amino acid.

Table I. Electrometric Titration of a Solution of Latex Amino Acid[a] with a Glass Electrode

Potentiometer Reading at		Electromotive Force	pH from Calibration Curve	Normality of NaOH in Amino Acid Soln.	Normality of Aqueous NaOH at Same pH	Corrected Normality of NaOH
Null point	0.5810 volt					
517.5	725	0.4147	8.83	0.0028	....	0.0028
555	725	0.4448	9.23	0.0056	....	0.0056
576	725	0.4616	9.44	0.0082	....	0.0082
595	722	0.4788	9.68	0.0119	....	0.0119
621	722	0.4997	9.99	0.0158	....	0.0158
656	722	0.5279	10.43	0.0197	0.0003	0.0194
705	722	0.5673	11.09	0.0238	0.0013	0.0225
730	722	0.5874	11.40	0.0272	0.0028	0.0244
756	722	0.6084	11.89	0.0326	0.0082	0.0244
768	722	0.6180	12.23	0.0448	0.0180	0.0268

[a] 0.5436 gram per 250 cc.

The titration (data given in Table I) was carried out with 50 per cent carbonate-free sodium hydroxide. The concentration of sodium hydroxide after each addition was found by removing 10-cc. samples and titrating them with standard hydrochloric acid, and the pH by means of a glass electrode. The results are plotted in Figure 1. The true titration curve obtained by methods well recognized shows that the end point is at 0.0244 *N*. Here the concentration of organic material was:

$$\frac{1000 \times 0.5436 \times 4}{1001.3} \text{ grams per liter}$$

Hence the molecular weight of the compound is:

$$\frac{1000 \times 0.5436 \times 4}{1001.3 \times 0.0244} = 89.0$$

This value, which can be taken as the molecular weight rather than merely the combining weight (since, under the conditions of the vacuum distillation, only monobasic, amino acid esters could have distilled) agrees with alanine (molecular weight 89.1). A rough estimation of the molecular or combining weight can be obtained from the slope of the curve at the half-titration point by means of the approximate formula:

$$\frac{d[B]}{d(\mathrm{pH})} = 0.5758[S]$$

Where B = equivalents of NaOH added
S = total amino acid in all forms
Square brackets refer to equivalent concentration

The reciprocal of slope at the half-titration point is 0.0146. Hence, molarity = 0.0146/0.5758 = 0.0254, and the approximate molecular weight = (0.5436 × 4)/0.0254 = 86.

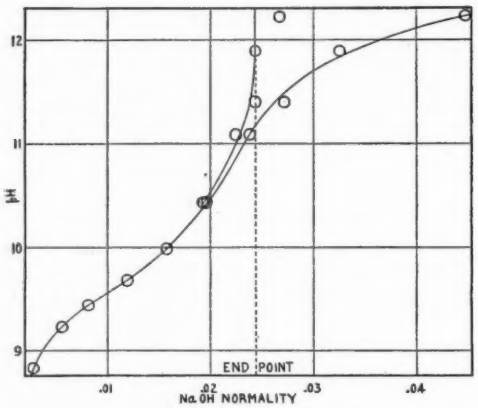

FIGURE 1. TITRATION CURVE OF LATEX AMINO ACID AT 25° C.

At the half-titration point the pH is 9.71. This gives K_a (25° C.) = 1.95×10^{-10}. The same electrode gave the same value for K_a for a sample of *d*-alanine (data not given). The value of K_a (25° C.) for alanine reported by Branch and Miyamoto (*1*) is 2.06×10^{-10}.

The long method reported here for the extraction of an amino acid from latex is probably not the simplest that could be devised; it was adopted chiefly because it seemed the one most likely to give definite results.

It would be useful to know whether the amino acids are present in the latex immediately after its removal from the tree or are produced by alkaline hydrolysis of proteins. In this connection it is perhaps worthy of note that, although the available evidence is in favor of the view that latex con-

tains several amino acids, so far only alanine has been isolated in sufficient quantity to obtain definite identification. Evidence of the presence of others is meager, and it is possible that *d*-alanine is a natural constituent of latex and that the proteins are not hydrolyzed to any great extent.

Work in Sumatra, Dutch East Indies, by one of the writers resulted in the extraction of a small quantity of a similar amino acid from a sample of dried serum solids obtained by spraying the serum left from acetic acid coagulation of some fresh unpreserved latex. Owing to the smaller amount it could not be purified to the same extent, and its melting point was about 20° C. lower than that of the substance obtained here. The rotation in hydrochloric acid of this impure product was found to be $\alpha_D^{30} = +6.4°$. Emil Fischer gives $\alpha_D^{20} = +10.3$ for pure *d*-alanine hydrochloride.

Literature Cited

(1) Branch and Miyamoto, *J. Am. Chem. Soc.*, 52, 863 (1930).
(2) McGavack, J., and Rumbold, J. S., Ind. Eng. Chem., Anal. Ed., 3, 94 (1931).
(3) Whitby, G. S., Dolid, J., and Yorston, F. H., *J. Chem. Soc.*, 1926, 1448.

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Rubber Plasticity Control

Significance and Value of Recovery Measurement of Williams Plastometer

J. H. Dillon, Firestone Tire and Rubber Company, Akron, Ohio

THE original compression plasticity test for rubber, as developed by Williams (*14*), consisted in measuring the compressed height (y value) of a 2-cc. rubber sample after a standard time of compression under a 5-kg. load at a standard temperature. No account was taken of the increase in height—i. e., recovery, of the pellet after removal of the load. The distinction between plastic flow and pseudoplastic flow in the compression test, as applied to rubber, was first made by van Rossem and van der Meijden (*10*). They measured deformation of masticated rubber under load as a function of time of compression, and then removed the load and measured the recovery as a function of time. They showed that the ratio of the plasticity to the elasticity in the masticated rubber is a rapid function of temperature, increasing from zero at 16° C. to a very large value at 70°. Karrer (*6*) adopted the viewpoint of van Rossem and van der Meijden and suggested a definition of plasticity which included the total deformation of a pellet of standard dimensions under a standard compressive force acting for one second and its recovery after removal of the load. This definition, when given quantitative form, applied only to one type of measuring instrument, the Goodrich plastometer. Hence, the definition was purely arbitrary and was justified only in that it took account of one more variable than does the Williams y value. Karrer designed a plastometer (*7*) which was also adapted to the measurement of recovery, and in which the compressive force acted for a definite short-time interval. The plastometer platens were of the same type as those used by van Rossem and van der Meijden; that is, the platen faces were of the same area (one sq. cm.) as the ends of the cylindrical pellet. A simpler plastometer (*8*) which differed only in that it operated under a dead load was designed for control work.

The arguments of the various investigators (*6*, *10*, *12*) in regard to the significance of recovery in plasticity measurements have been of definite value in clarifying what had been a somewhat vague conception of plasticity among rubber technologists. Certainly the basic idea, as maintained by Karrer, van Rossem, and van der Meijden, that the Williams plastometer y value is a measure of both the plastic mobility and the elastic modulus of the rubber is correct. However, the proponents of the recovery measurement have neglected one important factor—namely, the dependence of elastic recovery upon speed of deformation. It has been shown by Dillon and Johnston (*3*), in connection with experiments on an extrusion plastometer, that elastic recovery is a rapid function of the speed of deformation of the rubber (rate of shear). Furthermore, it has been shown mathematically (*3*) that, for the Williams plastometer, the rate of shear for a given testing time varies inversely as the $^3/_2$ power of y. It has been shown also (*3*) that, for the Goodrich plastometer, the mean rate of shear is given by

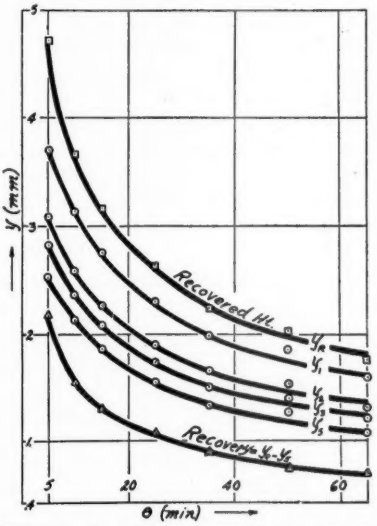

FIGURE 1. WILLIAMS PLASTOMETER INDICES AS FUNCTIONS OF TIME OF MILLING (θ)

Pale crepe; plastometer at 100° C.; cold 30.5 × 15.2 cm. mill

$$\frac{dv}{dy} = \frac{9RK}{16} y \qquad (1)$$

where R = original radius of pellet
y = separation of plates at time t
$K = \frac{1}{t}\left(\frac{1}{y^2} - \frac{1}{y_0^2}\right)$
y_0 = original height of pellet

Hence

$$\frac{dv}{dy} = \frac{9Ry}{16t}\left(\frac{1}{y^2} - \frac{1}{y_0^3}\right) \qquad (2)$$

For a given testing time, t, the mean rate of shear is a function of y for the Goodrich plastometer also. Thus the elastic recovery must be a rapid function of y value in both

types of compression plastometer. It follows directly, then, that the recovery measurement is not only a measure of the residual elasticity of the rubber but also of the plastic properties. It is to be expected, therefore, for a given rubber stock at least, that the y value and recovery measurements should correlate. This conclusion is verified by the results of the present investigation.

It would seem, because of the importance which recovery assumes in an academic sense, that the measurement of recovery should have practical importance in plasticity control testing. However, the author has been unable to find in the literature (*1–15*) any data to show that the measurement of recovery on different batches of a given stock provides any information in addition to that yielded by the simple measurement of y value. Garvey (*4*) has presented some inter-

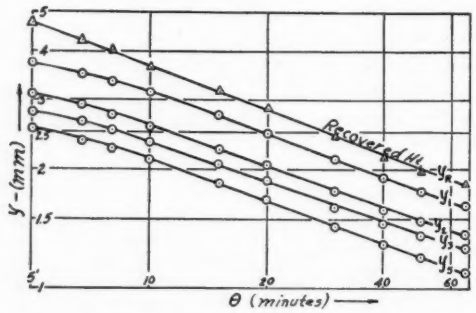

FIGURE 2. WILLIAMS PLASTOMETER INDICES AS FUNCTIONS OF MILLING TIME (θ), USING LOGARITHMIC COÖRDINATES

Pale crepe; plastometer at 100° C.; cold 30.5 × 15.2 cm. mill

esting results on the relation between the retentivity and softness, as measured by the Goodrich plastometer, as a function of degree of vulcanization. He plotted the softness against the retentivity for several testing temperatures. The resulting straight lines have different slopes, depending on the time of cure. These particular results are hardly applicable to plasticity control testing, although they suggest that the measurement of recovery at two or more temperatures may be very useful in this regard. He has also stated that the retentivity-softness relation is useful in differentiating tough, crude rubber from scorched rubber. Inasmuch as these latter results have not yet been published, they cannot be considered here. Karrer, Davies, and Dietrich (*8*) have given experimental data which show that recovery and y value, as measured by the Goodrich plastometer, are not

simply related for different stocks. The data do show, however, that for crude rubber and gum stocks there is very good correlation between recovery and y value. Furthermore, the curves giving the relation between recovery and time of milling are similar to the curves giving y value (softness) as a function of time of milling. Since plasticity control consists mainly in comparing the plastic properties of different batches of a given stock, it was necessary to perform some simple experiments described in this paper in order to decide whether or not factory control information could be obtained from recovery measurements with a Williams plastometer which could not be gained through measurement of y value alone.

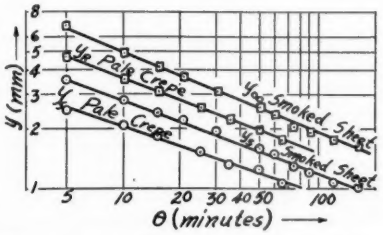

FIGURE 3. WILLIAMS PLASTOMETER INDICES AS FUNCTIONS OF MILLING TIME (θ)

Pale crepe and smoked sheet; plastometer at 100° C.; cold 30.5 × 15.2 cm. mill

EXPERIMENTAL PROCEDURE

Two somewhat different methods of measuring recovery were employed. The first consisted simply in obtaining the y value, removing the compressed pellet from the press exactly at the end of the 5-minute compression period, and measuring the recovered thickness of the pellet 24 hours later at room temperature, with an ordinary thickness gage. This recovered thickness was recorded as y_∞.

The second method, which is more accurate than the first, is as follows: The thickness gage was placed in the plastometer oven and allowed to come up to the testing temperature (85° C. for compounded stocks, 100° C. for crude rubber and master batches). The whole test was performed in the same oven at constant temperature. The 2-cc. cylindrical pellet (not preheated) was placed between the platens of the plastometer and compressed for 5 minutes. Readings of the plastometer gage giving the thickness of the pellet ($=y$) were taken at various intervals during the compression (usually after 1, 3, and 5 minutes of compression). Exactly at the end of the 5-minute compression period, the y_5 value was noted, and the load was removed from the pellet which was transferred quickly to the thickness gage (from which the loading weight and lifting handle had been removed) and allowed to recover for 5 minutes. The recovered thickness was then recorded as y_R.

The second method appears superior to the first in that certain errors introduced by uneven shrinkage of the pellets

during cooling are eliminated. In practice, however, it was found that the results of the two methods correlated within the limits of experimental error.

Only the quantities y_5 and y_R or y_∞ were considered in this work. The recovery difference function, $(y_R - y_5)$ or $y_\infty - y_5$), was not employed for the following reasons: It has been found that, when the recovery $(y_R - y_5)$ was of the same order of magnitude as y_R, $(y_R - y_5)$ varied in practically the same manner as y_R alone. When $(y_R - y_5)$ was much smaller than y_R, $(y_R - y_5)$ varied more rapidly than y_R, but the percentage error in $(y_R - y_5)$ was much larger than in y_R. This is to be expected, of course, for the same total error exists in $(y_R - y_5)$ as in y_R. Thus, for $y_R - y_5 \ll y_R$, the value of $(y_R - y_5$ is of the same order of magnitude as the probable error in y_R and calculation of the recovery has very little meaning.

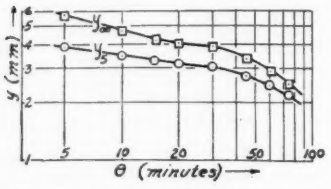

FIGURE 4. WILLIAMS PLASTOMETER INDICES AS FUNCTIONS OF MILLING TIME (θ)

Smoked sheet; plastometer at 100° C.; hot 30.5 × 15.2 cm. mill

EMPIRICAL RELATIONS BETWEEN WILLIAMS PLASTOMETER RESULTS AND TIME OF MILLING

The plastic state of a finished rubber stock is determined mainly by three factors: Initial plastic state of the crude rubber, nature and amount of mechanical treatment given the rubber, and amount of premature vulcanization (set-up) introduced during processing. In order to study the significance of the Williams plastometer indices (y value and recovery), it was necessary to determine the dependence of the indices upon these three fundamental factors.

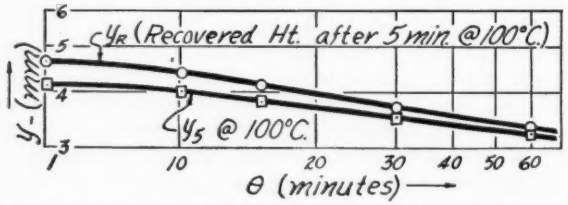

FIGURE 5. WILLIAMS PLASTOMETER INDICES AS FUNCTIONS OF MILLING TIME (θ)

Carbon-black master batch; plastometer at 100° C.; cold 30.5 × 15.2 cm. mill

The effect of mechanical treatment upon y value and recovery was studied by investigating their relations to time of

milling. Samples of the crude rubber or rubber compound were placed on the rolls of a cold 12 × 6 inch (30.5 × 15.2 cm.) laboratory mill (ratio of roll speeds = 1.10) and were cut for 120 minutes or less. Samples were taken from the batches at intervals during the milling process, and measurements of y value (y_1, y_2, y_3, y_5) and recovered y value (y_R or y_∞) were made as described under Experimental Procedure. Two determinations were made on each sample. The average y values, recovered y value, and also the recovery ($y_R - y_5$) for a 1000-gram batch of pale crepe are plotted as functions of milling time in Figure 1. The curves are of the familiar form and are all approximately parallel. These same data are plotted logarithmically in Figure 2; parallel straight lines result in the interval of milling times 8–65 minutes.

Figure 3 shows another logarithmic plot of these results for pale crepe, and also of those for a 1000-gram batch of smoked sheet. The curves are linear and have nearly the same slope.

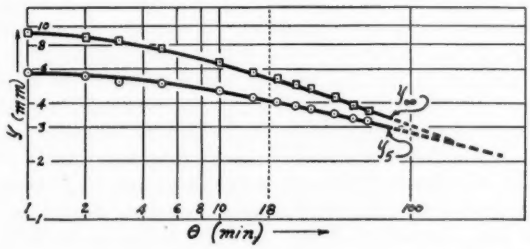

FIGURE 6. WILLIAMS PLASTOMETER INDICES AS FUNCTIONS OF MILLING TIME (θ)

Smoked sheet; plastometer at 100° C.; water-cooled 213.4 × 61 cm. mill

The linear form of these parallel logarithmic curves suggests the existence of an empirical equation of the form:

$$y_t = b_t \Theta^m \qquad (3)$$

where y_t = y value or recovered y value (at testing time t) corresponding to a milling time, Θ
b_t = a constant characteristic of testing time t
m = a constant characteristic of these types of rubber on this particular cold mill

Equation 3 applies to rubber on a cold 12 × 6 inch (30.5 × 15.2 cm.) mill. The slope of the curves gives the value of m as −0.364.

The form of these logarithmic curves may be interpreted to mean, for this particular case, that both y_5 and y_R obey the

same law expressed by Equation 3 —i. e., are the same functions of the parameter, Θ. Thus, for detection of plasticity variations in massed crude rubber due to different amounts of breakdown under these particular conditions, measurements of y value and recovery tell the same story. In other words, in so far as it is desired to detect varying amounts of a given type of mastication of gum rubber, measurement of recovery appears to be a superfluous operation.

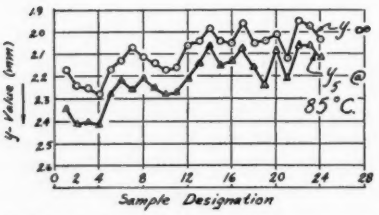

FIGURE 7. DIRECT CORRELATION BETWEEN y VALUE AND RECOVERY

Twenty-six factory batches of a tube stock; Williams plastometer at 85° C.

A similar logarithmic plot for smoked sheet on a hot 12 × 6 inch (30.5 × 15.2 cm.) laboratory mill is shown in Figure 4. The data were obtained as follows: A batch of smoked sheets was cut on the laboratory mill with no cooling water in the rolls and the y_5 and y_∞ values were measured on samples taken from the batch at various intervals during the milling. The curves are approximately linear, though not quite parallel in the interval of milling times 5–30 minutes. At $\Theta = 30$ minutes, the slopes of the curves change greatly, and they are no longer linear. However, the curves are similar and it seems that, for this case also, no information in addition to that furnished by measurement of y_5 is gained by measuring y_∞. It is true that the curves indicate that y_∞ gives a slightly more sensitive measure of amount of mastication than does y_5. This advantage is nullified, however, by the larger chance of error in y_∞ or y_R, whichever is measured.

In order to determine whether a highly pigmented rubber stock behaves in the same manner on the mill as does pure gum, a carbon-black master batch (28 volumes of carbon black, 100 volumes of rubber) was milled as follows: A 1200-gram sample of the master batch was placed on the hot laboratory mill and cut for 5 minutes. The cooling water was then turned on and the batch was milled for 55 minutes more on the cold mill. Samples were taken at appropriate intervals and y_5 and y_R were measured on them. The logarithmic curves are given in Figure 5. The curves are approximately linear but not parallel. It is possible in this case, therefore, that recovery is a slightly more sensitive measure of degree of breakdown than is y value alone; i. e., the quantity, m, is larger for the $(y_R - \Theta)$ curve than for the $(y_5 - \Theta)$ curve. Except for this slight advantage in sensitivity, however, y_R and y_5 obey the same type of power law in Θ. Hence they cannot be said to measure greatly differing properties, and it

is doubtful whether the measurement of both y value and recovery is justified from a practical control standpoint.

All the results thus far discussed have been obtained from rubber on one particular laboratory mill. By no means is it to be concluded that such results will apply accurately to the regular factory milling procedure. In fact, the logarithmic y-Θ curves for a 300-pound batch of smoked sheet on a water-cooled 84 × 24 inch (214 × 61 cm.) mill (front roll speed = 115 feet per minute, back roll speed = 124 feet per minute) were somewhat different from those for the cold laboratory mill (Figure 6). Here the curves were neither linear nor parallel. In fact, they appeared to be approaching each

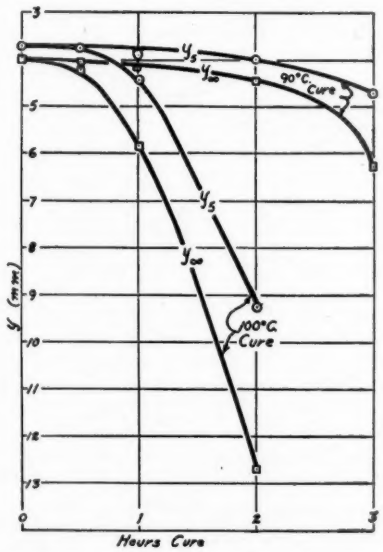

FIGURE 8. WILLIAMS PLASTOMETER INDICES AS FUNCTIONS OF TIME OF CURE

Tread stock (26 per cent carbon black by volume on the rubber, accelerated by mercaptobenzothiazole); plastometer at 100° C.

other, as shown by the extrapolated dotted lines; i. e., the rubber was approaching the true dead-milled state where the recovery becomes negligibly small. The rubber is usually batched off at Θ = 18 minutes. Thus, from a practical standpoint no great advantage of the recovered y_∞ measurement over the y_5 measurement appears in this case, for the curves are of similar form in the interval 0–18 minutes.

DIRECT CORRELATION BETWEEN y VALUE AND RECOVERED y VALUE FOR COMPOUNDED STOCKS

A number of correlations have been made on factory batches

of regular compounded stocks. For example, in Figure 7 are shown the y_5 and y_∞ data for twenty-four batches of a tube stock accelerated by an aldehyde amine type of accelerator. No significant departures from good correlation appear. Thus, no practical advantage to be gained from the y_∞ measurement is apparent from this type of investigation.

Williams Plastometer Results in Relation to Set-up

Premature vulcanization (set-up) of rubber stocks, resulting from abnormally high milling temperature, too high tub-

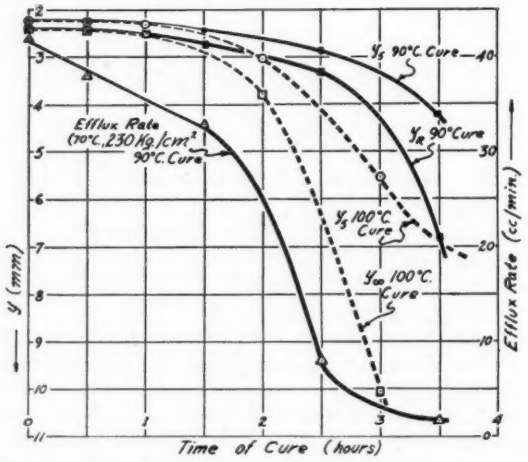

Figure 9. Williams and Extrusion Plastometer Indices as Functions of Time of Cure

Tube stock accelerated by an aldehyde amine; Williams plastometer at 100° C.; extrusion plastometer pressure = 3270 pounds per square inch (229.9 kg. per sq. cm.) at 70° C.

ing speeds, improper compounding, or storage in large rolls, is another important factor to which the results of a plasticity control instrument must be sensitive. In order to compare the y value and recovered y value measurements with respect to the degree of set-up, samples of typical tread and tube stocks were heated at 90° and 100° C., for times varying from 0 to 3.5 hours, and plasticity measurements were made on them. Figure 8 shows the indices y_5 and y_∞ plotted as functions of time of cure for a tread stock (26 per cent carbon black by volume; accelerator, mercaptobenzothiazole). The curves for a given curing temperature are of nearly the same form. Here again it may be claimed that y_∞ and the recovery $(y_\infty - y_5)$ vary more rapidly with time of cure, and furnish therefore a more sensitive measure of set-up. Unfortunately, percentage calculations of changes in y_5, y_∞, and $(y_\infty - y_5)$ have very little significance. Hence, no quantita-

tive proof can be given to show which of the indices is the most sensitive in respect to any variable. It should be remembered, however, that the recovery measurement is subject to the inaccuracies inherent in any quantity, which is the small difference between two large quantities. Furthermore, in measuring y_∞ or y_R, an additional measuring operation is required, and hence y_∞ or y_R is subject to more error than is y_5. This reasoning is fully borne out by experience.

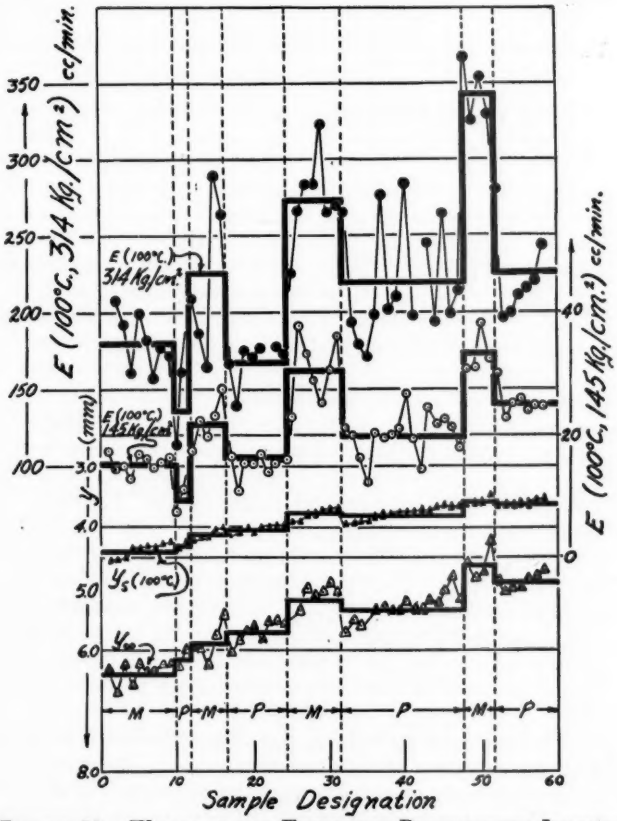

FIGURE 10. WILLIAMS AND EXTRUSION PLASTOMETER INDICES AS MEASURED ON FIFTY-EIGHT BATCHES OF PLASTICATED AND MILL-MASSED SMOKED SHEET

Williams plastometer at 100° C.; E = efflux rate of extrusion plastometer; heavy horizontal lines give average data in each group.

A similar set of curves for a typical tube stock accelerated by an aldehyde amine is shown in Figure 9. The same remarks made in connection with the curves of Figure 8 apply also here.

Another curve is plotted in Figure 9, obtained with the same samples (90° C. cure) with an extrusion plastometer described elsewhere (*3*). The efflux rate (volume extruded in

unit time at a constant driving pressure and temperature, as measured in the extrusion plastometer, varies much more rapidly with time of cure than do the Williams plastometer indices.

Excluding the results of the extrusion plastometer from the discussion, these data fail to show that the recovery measurement of the Williams plastometer is superior to the usual y value measurement in detecting set-up in these typical stocks.

Plasticity Measurements on Plasticated and Mill-Massed Rubber

Two distinctly different types of masticating machines are employed in modern rubber plants, mills, and plasticators. The experience in this plant has been that rubber, plasticated in the Gordon machine, which gives the same y_5 value with the Williams plastometer as a sample of mill-massed rubber, appears much stiffer in factory processing operations than the mill-massed rubber. Thus, there is need of a method for detecting the difference, which certainly exists but is not revealed by the Williams plastometer, between the plastic properties of plasticated and mill-massed rubber.

In order to study this phenomenon, fifty-eight samples of plasticated and mill-massed smoked sheet were selected in a range of y value (3.5 to 4.5 mm.), and three types of plasticity tests were made on them. The Williams plastometer indices y_5 and y_∞ were measured as described under Experimental Procedure. Plasticity measurements at 100° C. were also made with the extrusion plastometer (*3*) with two driving pressures, 2060 and 4480 pounds per square inch (145 and 316 kg. per sq. cm.). The results are plotted in Figure 10 in the form of correlation curves. The data are separated into groups according to y_5 value and the type of the masticating process employed—i. e. plasticated (P) or mill-massed (M). The averages of the readings in the various groups are indicated by the heavy horizontal lines.

It is quite clear that the y_5 measurements do not correlate with the extrusion plastometer results. The latter are seen to be much more sensitive to variations in plasticity than are the Williams plastometer indices. The extrusion plastometer results indicate definitely that mill-massed rubber is softer than plasticated rubber yielding the same y_5 value, thus agreeing with conclusions based on factory experience. The y_∞ curve is contradictory, indicating that mill-massed rubber is softer than plasticated rubber of a given y_5 value in two cases and the reverse in two others. Hence, it seems reasonable to conclude that, although the y_∞ measurement is more sensitive than the y_5 measurement and agrees in part with factory experience whereas the y_5 measurement does not, still it does not furnish the consistently accurate information given by the extrusion plastometer results.

Conclusion

The experiments described in this paper were undertaken in an effort to discover under what conditions the recovery measurement has practical value in plasticity control testing. No conditions were found where the recovery measurement yielded any important practical information which could not be gained by measurement of y value alone. It must be borne in mind that no experiments of this nature can be considered as perfectly general. Certain cases, not specifically included in the experimental conditions employed, may exist where measurement of recovery has definite practical value. Furthermore, great caution should be exercised in applying these results to any types of compression plastometers other than the standard Williams instrument with which the tests were made.

Acknowledgment

In conclusion the author wishes to thank N. Johnston and O. D. Cole for their suggestions which helped materially in carrying out this work, and N. A. Shepard under whose direction this work was done.

Literature Cited

(1) Dietrich, E. O., Ind. Eng. Chem., **21**, 769 (1929).
(2) Dietrich and Davies, *Ibid.*, Anal. Ed., **3**, 297 (1931).
(3) Dillon and Johnston, *Physics*, **4**, 225 (1933).
(4) Garvey and White, Ind. Eng. Chem., **25**, 1042 (1933); Garvey and Thompson, *Ibid.*, **25**, 1292 (1933).
(5) Grenquist, E. A., *Ibid.*, **22**, 759 (1930).
(6) Karrer, E., *Ibid.*, **21**, 770 (1929).
(7) Karrer, E., *Ibid.*, Anal. Ed., **1**, 158 (1929).
(8) Karrer, Davies, and Dietrich, *Ibid.*, **2**, 96 (1930).
(9) Peek, R. L., *J. Rheol.*, **3**, 345 (1932).
(10) Rossem, van, and Meijden, van der, *Rubber Chem. Tech.*, **1**, 393 (1928).
(11) Scott, J. R., *Inst. Rubber Ind. Trans.*, **7**, 169 (1931).
(12) Usherwood, G. W., *Ibid.*, **8**, 227 (1932).
(13) Vries, O. de, *Arch. Rubbercultuur*, **9**, 260 (1925).
(14) Williams, Ira, Ind. Eng. Chem., **16**, 362 (1924).
(15) Winklemann and Croakman, *Ibid.*, **22**, 865 (1930).

[Translated for Rubber Chemistry and Technology from Le Caoutchouc et La Gutta-Percha, Vol. 31, No. 363, pages 16,765–16,768, May 15, 1934.]

The Perchloric Method for the Determination of Sulfur in Rubber

Ernest Kahane

The problem of the determination of sulfur in rubber has been dealt with extensively in the literature, and it seems as if discussions and descriptions of new technic are nowhere nearly ended yet.

The determination is so essential, and its rapid and precise execution is of such importance in industrial technic, that efforts in this direction should not be regarded as wasted.

In 1926 and in 1927 *Le Caoutchouc et La Gutta-Percha* contained two articles[1,2] in which the present author discussed the conditions of the determination of sulfur in rubber and then proposed the use of a new oxidizing mixture, not mentioned previous to that time, which involved the destruction of organic substances by perchloric acid.

This method consisted simply in the attack on a 1-gram sample of rubber by 10 cc. of nitric acid (d. 1.39) and 5 cc. of perchloric acid (d. 1.61). Upon heating, attack by the nitric acid takes place, and this is followed by evaporation of the excess nitric acid, then at a little higher temperature there is an attack by the perchloric acid, which oxidizes the rest of the organic substance completely.

This publication was concerned much more, in the determination of sulfur by the perchloric method, with the general idea of the destruction of organic substances than it was with the precise details of carrying it out. The technic had been studied somewhat superficially, as is shown by the text of the article itself.

Later the application of this technic (in collaboration with Lematte and Boinot) to vegetable and animal substances[3] demonstrated that although in this particular case satisfactory results can be obtained by means of a mixture of fuming nitric acid and perchloric acid, this is not true when commercial concentrated nitric acid (d. 1.39) is used alone, the use of which the present author had suggested for the analysis of rubber.

Because of its convenience and its rapidity, the nitric-perchloric technic offered such advantages over the methods ordinarily used that numerous rubber chemists studied it or applied it. Among these chemists, there may be mentioned in particular Mackay[4] and Wolesensky,[5] who carried out a somewhat severe critical study in which they demonstrated the shortcomings of the method. These authors showed that according to the particular conditions of the procedure more or less important losses of sulfur may occur. None the less they appreciated the merits of the perchloric method and, far from giving it up, tried to reduce the errors arising from faults in the method. The proposed modifications consist, in the technic of Wolesensky, in carrying out a prolonged attack on the water bath before carrying out the perchloric acid attack, and in the technic of Mackay, in utilizing an enormous excess of the oxidizing mixture and in substituting ordinary fuming nitric acid for ordinary nitric acid and finally in adding bromine. By means of these precautions, which in both cases detract from the original simplicity of the method, satisfactory results appear to have been obtained.

The systematic development of analytical applications of perchloric acid has led the present author to resume the critical study of the determination of sulfur following attack by nitric-perchloric acid. This work, which was carried out in collaboration with Mme. Kahane, has led to the publication of an article which deals with the general principle of the method,[6] with its application to certain organic substances,[7] and with its application to medicinals containing sulfur.[8] In the field of industrial chemistry it is proposed to prove the validity of this method in two particularly important cases, *viz.*, that of rubber and that of fuels.

The author of this article should not be held solely responsible for the imperfection in the technic previously described. The numerous authors who have studied methods of the determination of sulfur in rubber in the wet way seem for the most part to be much more concerned with the complete destruction of the organic material following the attack by nitrogen than with losses of sulfur which may take place through its volatility. The result of all their work gives a clear impression that the determination of sulfur in rubber cannot be carried out by a simple treatment with nitric acid because of the retention of the sulfur in an organic

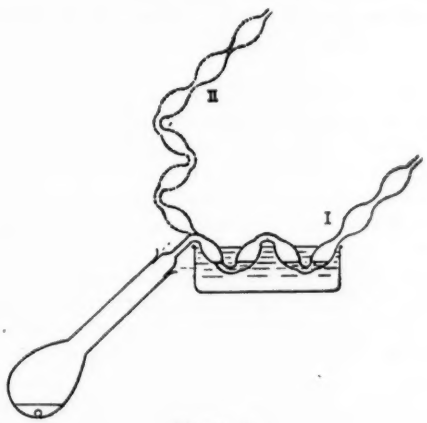

Figure 1

form in the liquid obtained. The different methods proposed in general have as their object the destruction of the sulfurated products, the presence of which had been suspected. This is not the place for a detailed discussion of the methods proposed, and the author knows full well that there are exceptions, such as the methods of Waters and Tuttle, where the addition of bromine to the fuming nitric acid causes, when carried out by a very careful technic, the retention of the sulfur which would otherwise escape in the volatile form during the first stage of the disaggregation.

In a preliminary work to which reference has been made, an attempt was made to show that the complete destruction of organic substances is superfluous, and that by means of certain precautions in rinsing it is possible to dispense with the complete destruction. It is advisable to consider only one of the various aspects of the problem, namely, that of the destruction of organic material. It seemed evident from the literature, though incorrect, that a method involving oxidation by nitric acid cannot lead to any appreciable evolution of volatile sulfurated compounds. However, such is the case, since in the determination of the sulfur in bio-

logical substances, it is only by the use of nitric acid that comparable results have been obtained by the present author. Since perchloric oxidation is complete, in both cases the deficiency found when ordinary nitric acid is used can only be attributed to an evolution of volatile sulfurated compounds.

The simple adaptation to the analysis of rubber of this increase in concentration of nitric acid would not have been possible, even if it had been entirely effective, because of the violence of the attack upon certain substances by fuming nitric acid. For example, in the case of ebonite the material takes fire when it is heated with fuming nitric acid. The same is true in the case of rubber containing less sulfur, and here the state of division of the sample plays an extremely important role. Certain differences between the results of Wolesensky and the present author must be attributed to the fact that the former used in his tests a rubber in powdered form whereas the present author used rubber cut into 2 to 3 mm. cubes.

Aside from this purely technical inconvenience, which could have been remedied, it is necessary to point out first of all that the fuming nitric acid technic is not entirely efficacious and that in this method too there is entrainment of sulfur in a volatile form.

As has been shown in various cases, the vapors evolved contain considerable quantities of hydrogen sulfide and sulfurous gas.

In a certain number of special cases, the sulfur which entrained in this way was determined, and it was proved that the quantity was far from negligible. This determination was made with the apparatus which will be described later, but it could be done just as well in any type of reaction flask having a bubbler. The vapors evolved bubble into a solution of iodic acid and the sulfur is fixed. The liquid obtained is then attacked by a nitric-perchloric acid mixture under conditions which cannot be questioned and which are described later, the iodic acid is reduced, and the sulfuric acid is determined by precipitation in the form of barium sulfate.

By carrying out the attack on 1 gram of a commercial rubber containing 1.65 per cent of sulfur by 15 cc. of fuming nitric acid, and by continuing this attack until almost two-thirds of the liquid was evaporated, it was found that 10.0 mg. of barium sulfate, *i. e.*, 8.3 per cent of the total sulfur, were formed at the expense of the sulfur entrained in the bubbler. A second treatment with fuming nitric acid, carried out under the same conditions, on the residue of the preceding operation, gives 1.6 mg. of barium sulfate, *i. e.*, 1.3 per cent of the total sulfur. A series of experiments of this sort showed that the phenomenon is quite general, and that the presence of a large excess of fuming nitric acid is not a sufficient guaranty of the complete oxidation of the sulfur.

It should be added that it is not necessary to assume that this sulfur is entrained in the form of a volatile organic derivative in order to account for this phenomenon, since it was observed in the same way and with even greater intensity in the attack by fuming nitric acid on sulfides, sulfites, hyposulfites, and on uncombined sulfur itself.

Apart from these considerations and, as mentioned above, in a number of special cases, hydrogen sulfide and sulfurous gas were detected in the reaction gas, by their characteristic reactions. The criticisms of the method which was described by the present author seven years ago were justified, and a technic was sought which would give greater satisfaction.

The expedients which have been proposed at different times in order to obtain a quantitative oxidation are effective only at the expense of a scrupulously minute technic; it may even be said that under ordinary circumstances, they are ineffective. Thus the addition of bromine, hydrogen peroxide, arsenic acid, etc., did not

make it possible to prevent the liberation of sulfurous gas and hydrogen sulfide satisfactorily. This is not surprising when it is considered that it is necessary to carry out the treatment with bromine for 12 hours before the treatment with nitric acid in the classical method of analysis of the mixture.

It was considered *a priori* that long and delicate procedures are unsuitable for practical industrial analysis. The general method described by the author and Mme. Kahane takes into consideration practical requirements, but it was possible to develop it only by sacrificing the extreme simplicity of the original method. Not only was it recognized that the addition of a reagent more "immediately reactive" than are nitric and perchloric acids was necessary, but it was also recognized that this addition does not diminish sufficiently the losses of sulfur, and the apparatus had to be supplemented by a bubbler containing the same reagent.

The reagent chosen was iodic acid, which oxidizes the hydrogen sulfide and the sulfurous gas quantitatively and rapidly without the necessity of a very complicated bubbling system.

The apparatus used was especially devised to meet this need. It is simple, sufficiently rugged, is well adapted to industrial analysis and to a series of analyses. Thanks to the arrangement of the bubbler, the automatic displacement and rinsing of the latter are easily carried out.

Apparatus

The apparatus used, which is called a "flask with W-shaped bubbler"[9] is made up of an ordinary 500-cc. Kjeldahl flask, on the neck of which is ground a hollow stopper carrying a tube bent four times in the shape of a W, the arms of which are blown into bulbs in the shape of elongated olives and of a volume of 20 cc. The first three bends of the W have a single bulb, while the fourth bend is longer and contains three bulbs.

The emptying and rinsing of this bubbler are effected in a very convenient manner, *i. e.*, the Kjeldahl flask on a support is inclined at 45° so that the bubbler occupies position I during the reaction. If necessary, the bubbler is immersed in a crystallizing pan of cold water so that by cooling in this way its condensing action is more effective.

When the reaction is complete and it is necessary to combine the sulfuric acid in the bubbler with the reaction liquid, the bubbler is cooled for a minute and then turned 180° on the ground stopper so that it takes position II in the illustration. The inclination of the drops and the shape of the bulbs are such that the entire contents of the bubbler flow into the flask. When the liquid is boiled, the first vapors condense in the bubbler and in returning to the flask they rinse the bubbler effectively.

Procedure

A sample of rubber of about 1 gram, weighed exactly, is placed in the Kjeldahl flask, 0.5 cc. of 10 per cent solution of iodic anhydride and 20 cc. of a mixture of two parts of perchloric acid (d. 1.61), and one part of nitric acid (d. 1.39) are then added.[10] A glass bead is placed in the flask to regulate boiling. The bubbler is immediately fixed in position I of the illustration by the free branch, into which 0.5 cc. of iodic acid solution and enough water to close the bent tube have been poured.

As this procedure involves a considerable volume of liquid, the bubbler cannot be sufficiently cooled with air, and it does not act satisfactorily enough as a condenser. Therefore a crystallizing pan of cold water is used for the cooling medium, and in this the bubbler is immersed.

At times the reaction starts spontaneously, but usually heat is required. Vapors of iodine are first evolved and then nitrous vapors, the greater part of which condense in the W tube. The excess nitric acid is distilled, the attack by the perchloric acid follows, usually somewhat vigorously, and this is indicated by an abundant evolution of gas. The chlorine evolved during the attack transforms the iodine in the bubbler into iodic acid, and thus allows it to continue to play its part with respect to the sulfur derivatives which might be evolved at this stage.

It is well to watch the procedure during the attack of unknown mixtures. When the attack by nitric acid has proceeded a little or when the perchloric acid is not sufficiently in excess, the reaction may be so lively as to require at times a decrease or even an interruption of the heating.

The end of the attack by perchloric acid is manifest by the fact that the boiling continues quietly and the liquid becomes colorless or yellowish.

The system is allowed to cool for half a minute before combining the liquid in the bubbler with the perchloric acid liquid. Unless this is done, there will be an intense evolution of vapor, which might cause loss of liquid or even blow out the ground stopper. In order to avoid such accidents, a sufficiently large volume in the bulbs has been provided to allow the air to enter again without loss of liquid.

After partial cooling, the bubbler is rotated 180° in the neck of the Kjeldahl flask.[11] In this way it takes position II of the illustration and, because of the elongated shape of the bulbs, the entire liquid flows into the flask.

The liquid is brought to boiling, and the vapors ascend into the bubbler where they condense, and in this way rinse it. The bubbler is then heated to remove the vapors. The water and nitric acid are eliminated, and a short time later the heavy white vapors from perchloric acid become visible, indicating the end of the operation.[12]

If the volume of perchloric acid remaining in the flask at the end of the operation does not exceed about 3 cc., it is useless to try to drive off part of it, and it should be allowed to cool. Otherwise the boiling is continued and the perchloric acid is concentrated to a volume of 2 to 3 cc.

The liquid is then transferred quantitatively to a cylindrical receptacle of 300-cc. capacity. The flask is washed with 50 cc. of water, and to the liquid is then added drop by drop a 10 per cent solution of hydrazine hydrate, which reduces the iodic acid to iodine and thence to hydriodic acid. The same result can be obtained, less easily perhaps, by the use of formaldehyde, which reacts rather violently, or by sodium iodide which liberates an enormous quantity of iodine. Were this reduction not carried out, the iodic acid would be precipitated at the same time as the sulfuric acid by barium chloride.

When the liquid becomes colorless, a drop of phthalein is added, then some 0.1 *N* sodium hydroxide until the color changes to red. The liquid is then made slightly acid with dilute hydrochloric acid, filtered if necessary, and precipitated at the boiling point by a 5 per cent barium chloride solution added dropwise. The precipitate of barium sulfate is collected, ignited, and weighed in the usual way.

The attack requires 15 to 20 minutes, the evaporation a little shorter time, the reduction of iodic acid and the neutralization some minutes more, so that the entire operation as far as the determination itself requires a little over one-half hour.

Results

The results obtained by the use of this procedure are from 10 to 20 per cent higher than results obtained by the usual method with nitric acid.

References

[1] Kahane, *Caoutchouc et Gutta-Percha*, **23**, 13,154 (1926).
[2] Kahane, *Ibid.*, **24**, 13,549 (1927).
[3] Kahane, *Comptes rendus Soc. Biol.*, **116**, 1211 (1927).
[4] *J. Soc. Chem. Ind.*, **49**, 233 (1930).
[5] *Ind. Eng. Chem.*, **20**, 1234 (1928); RUBBER CHEM. AND TECH., **2**, 45 (1929).
[6] *Comptes rendus*, **198**, 372 (1934).
[7] *Bull. soc. chim.*, [5] **1**, 280 (1934).
[8] *J. Pharm. chim.* (in press).
[9] Constructed by Cornette, 12 rue de Lanneau, Paris.
[10] The mixture must be used in great excess, both for correct results and for ease of attack. With refractory samples, it is preferable to use 25 cc. or more of the nitric-perchloric mixt.
[11] The ground-glass connection may stick, so it is advisable at the beginning of the analysis to moisten it with a drop of perchloric acid before putting the bubbler in place.
[12] This operation is not a simple concentration, because oxidizable substances may be distilled into the bubbler, and may there undergo an attack by perchloric-nitric acid at this stage.

[Reprinted from India Rubber Journal, Vol. 85, No. 11, page 296, March 18, 1933.]

Alcoholic Potash Extraction of Vulcanized Rubber

B. D. Porritt and J. R. Scott

In the analysis of vulcanized rubber, the estimation of matter extractable by alcoholic potash solution has long been applied, chiefly as a means of detecting and estimating factice. The test was originally made by weighing the rubber before and after boiling with potash solution, the loss in weight being taken as representing the factice content (cf. Weber, *The Chemistry of India Rubber*, London, 1919, page 245). Though this method has now been generally superseded by that in which the extract is acidified and the resulting fatty acids are extracted with ether and weighed, the older "loss in weight" method is still prescribed in some specifications for rubber goods.

It has long been recognized that the loss in weight is not an accurate measure of the factice content for the following reasons: (1) it is difficult to remove all the potash from the extracted rubber before weighing it (cf. Henriques, *Chem.-Ztg.* 18, 411(1894)), and (2) the potash extracts part of some mineral compounding ingredients, such as zinc oxide, litharge, and antimony sulfide (cf. Ditmar, *Die Analyse des Kautschuks*, Vienna, 1909, page 205).

It has been found that another possible source of serious errors in the "loss in weight" method is the action of the potash on light magnesium carbonate. If magnesium carbonate is boiled with alcoholic potash solution, it loses a considerable amount of its combined carbon dioxide and/or water. Thus in an experiment where 0.3 gram of the carbonate was boiled for 6 hours with 60 cc. of potash solution (KOH 5 g., water 5 cc., absolute alcohol 100 cc.), and then washed with alcohol, dried *in vacuo* and weighed, it was found to have lost 29.4 per cent of its weight. By igniting the residue to magnesium oxide, it was shown that the potash had not dissolved out any magnesium compounds, so that the loss in weight must be attributed entirely to loss of carbon dioxide and/or water.

As an example of the errors in analysis that may result from overlooking this action of alcoholic potash on magnesium carbonate, the following results for two samples of vulcanized rubber containing 18 per cent of light magnesium carbonate may be quoted (the two samples had the same composition, but were made from different batches of smoked sheet). In the alcoholic potash extraction, which was done on rubber not previously extracted with acetone, the following were determined: (1) loss in weight of the rubber (corrected for potash retained by the rubber); (2) fatty acids obtained by acidifying the extract and extracting with ether, and (3) mineral matter (zinc oxide and litharge) extracted by the potash.

	Percentages	
	I	II
Acetone extract (minus free sulfur)	1.35	1.55
Free sulfur	1.8	2.1
Fatty acids in potash extract	1.5	1.7
Mineral matter in potash extract	1.3	1.8
Loss in weight after extraction	10.4	11.0

According to these figures, the total matter extractable by potash solution, comprising organic matter, free sulfur and mineral matter, would be about 4.5 per cent and 5.0 per cent for I and II, respectively. The loss in weight is much greater than this, and the difference is far too large to be ascribed to non-rubber components of the raw rubber that might be extracted by the potash without appearing in the "fatty acid" item. The difference must therefore be due mainly to decomposition of the magnesium carbonate.

It is thus evident that the "loss in weight" method, applied to rubbers containing magnesium carbonate, gives an entirely erroneous idea of the magnitude of the alcoholic potash extract. The same may be true of rubbers containing whiting and other carbonates, but these have not yet been investigated.

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Hepteen	0.923	Thin liquid	20% the strength of Hepteen Base—same applications.
Trimene Base	1.142	Thick liquid	Footwear clothing, sheetings, sundries, mechanicals.
Trimene	1.027	Paste	Footwear, clothing, sheetings, sundries, mechanicals, sponge rubber.
Semi Rapid			
DiEsterex N	1.24	Powder	Footwear, sheetings, tires, tubes, mechanicals.
Safex	1.57	Powder	Tires, footwear, mechanicals.
Rapid			
Monex	1.40	Powder	Footwear, clothing, sheeting, wire, sundries, mechanicals.
Novex	1.365	Powder	Footwear, clothing, sundries.
Very Rapid			
CPB	1.17	Thin liquid	For room temperature vulcanization, or rapid vulcanizing at medium temperatures (175-200°F) or very rapid curing at higher temperatures.
DBA	1.029	Thin liquid	
ZBX	1.561	Powder	
ANTI-OXIDANTS			
Albasan	1.172	Flakes	Air cured goods, clothing, footwear, sheetings.
BLE	1.087	Liquid	Tires, tubes, soles, mechanicals, jar rings, footwear.
VGB	1.152	Resin	Wire, solid tires, mechanicals, rubber rolls.
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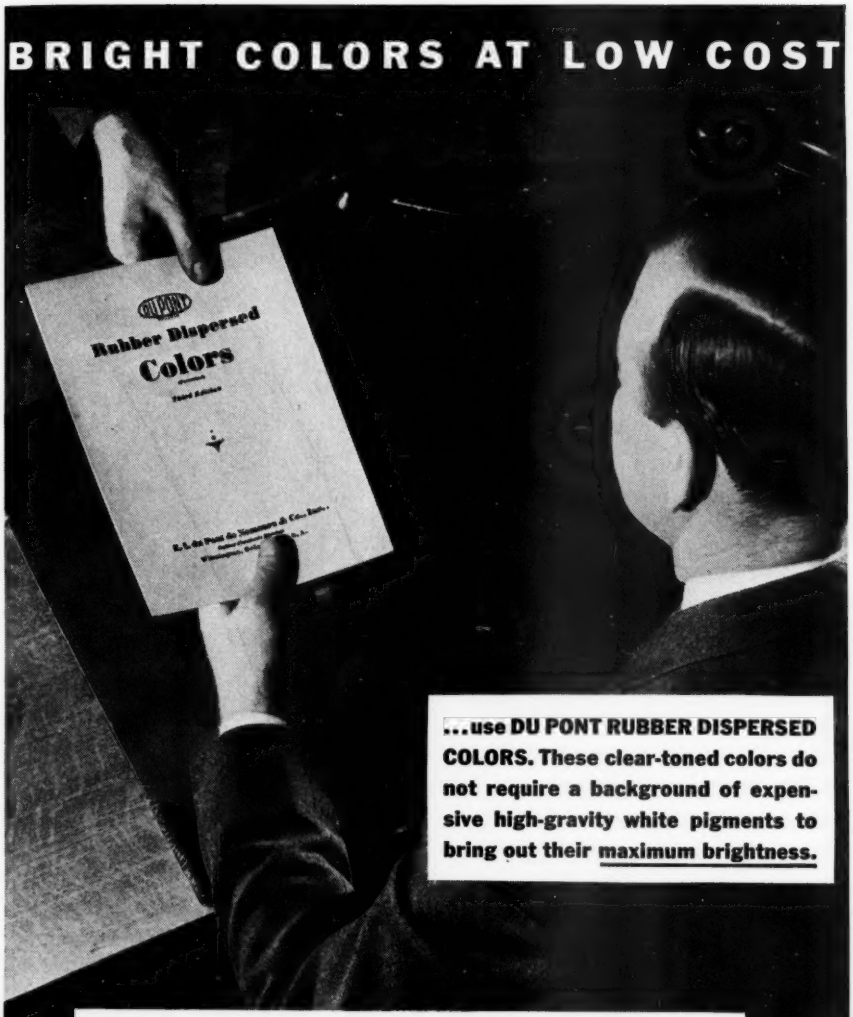

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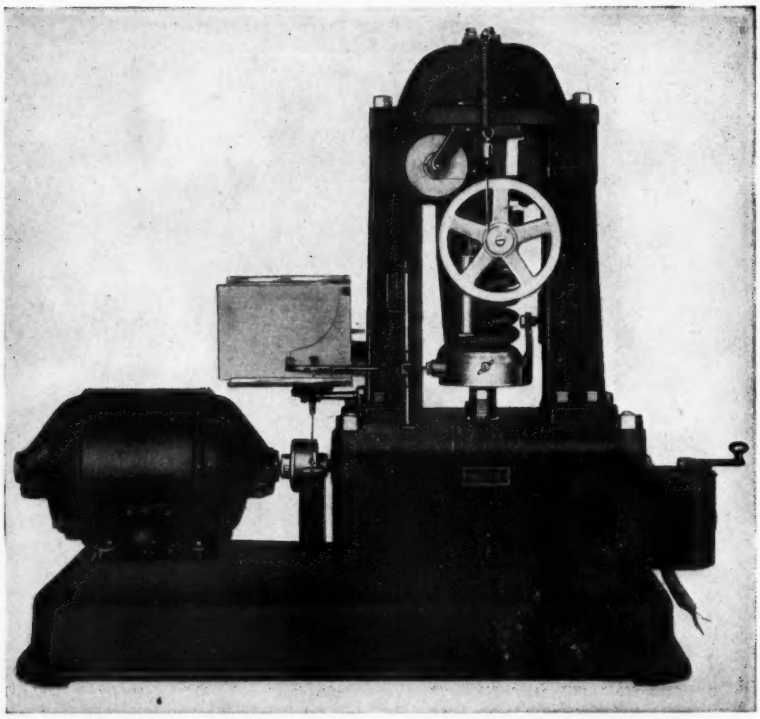

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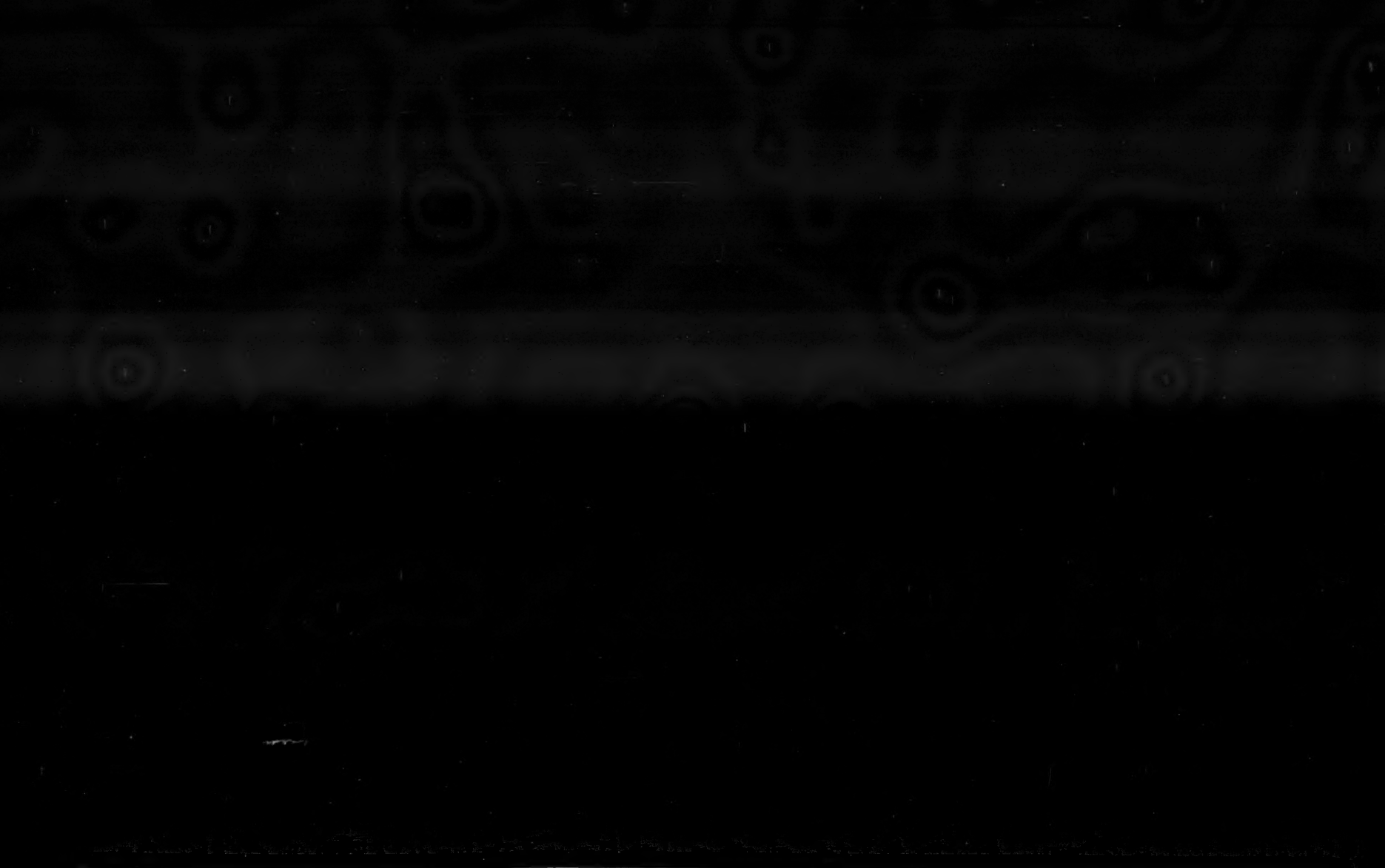
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